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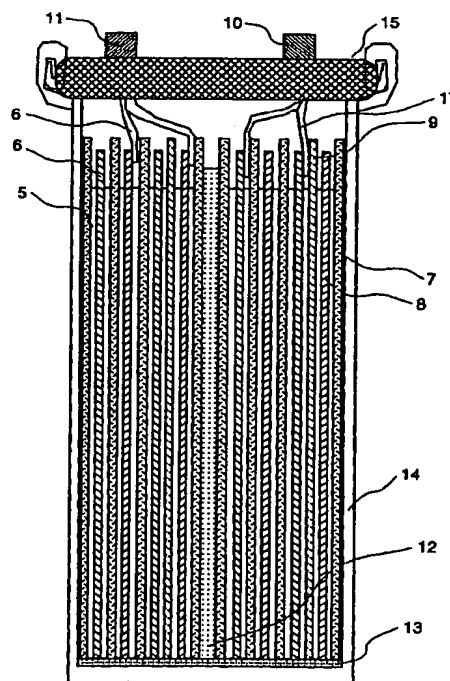
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(54) Lithium secondary battery, its electrolyte, and electric apparatus using the same

(57) Object of the present invention is to provide a lithium secondary battery, which is capable of terminating the operation of the battery safely accompanying with no rapid change in appearance, no gas generation, nor pressure change when any of overcharge, overdischarge, and abnormal temperature rise occurs with the secondary battery itself, its electrolyte, and electric apparatus using the battery as a power source.

A lithium secondary battery comprises a negative electrode (5, 6), which is capable of absorbing and desorbing lithium, a positive electrode (7, 8), which is capable of absorbing and desorbing lithium, and a non-aqueous electrolyte, wherein the non-aqueous electrolyte is solidified by a thermal reaction at a designated temperature.

FIG.1



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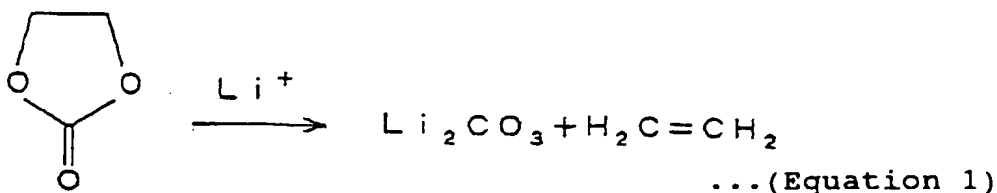
Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a lithium secondary battery, in particular, to a rechargeable lithium secondary battery improved in safety by having a self defensive safety function, an electrolyte for the lithium secondary battery, and electric apparatus using the same.

[0002] A lithium secondary battery has a high voltage, a high energy density, and superior storage performance and repeated charge-discharge characteristics. Therefore, the lithium secondary battery is used widely for portable electric consumer products. Furthermore, research and development for utilizing the batteries as power sources of electric vehicles and home power storage devices during night by increasing their size is being performed intensely. The lithium secondary battery is a product to be used widely in daily life as a clean energy source, which can be expected to have a significant advantage in preventing warming-up of the earth by releasing carbon dioxide and environmental pollution.

[0003] However, a flammable organic solvent is used in the battery in view of a reactivity with lithium and a restriction of potential window. Therefore, if a temperature of the battery is elevated by any means such as overcharging or exterior heating, the electrolyte causes a thermal runaway reaction, and generates a flammable gas to increase internal pressure of the battery. The gas is released to outside the battery can, and causes an ignition or, in the worst case, an explosion. Therefore, it is not emphasized too much to say that how widely the battery is used in the above objects depends on ensuring its safety. A carbonate group is generally used for the lithium battery, which uses carbon material for its negative electrode, because the carbonate group indicates preferable battery characteristics. In particular, five membered ring compounds such as ethylene carbonate and 1, 2-propylene carbonate are called as a main solvent and utilized as an indispensable solvent, because these compounds have a high dielectric constant, and readily dissociate lithium salts. These compounds cause a degradation reaction indicated by the following chemical equation (Equation 1), and generate a combustible gas, when they are heated or overcharged.



[0004] The internal pressure of the battery is increased by the combustible gas, the combustible gas is released from the battery can, and, in the worst case, an ignition and others are caused.

[0005] A method for preventing the ignition and explosion of the battery has been disclosed in JP-A-6-290793 (1994); wherein a solvent, which causes a polymerization reaction with LiPF_6 , i.e. a lithium salt, is mixed as an electrolyte solvent, in order to make the electrolyte cause no decomposition reaction, but a polymerization reaction when the temperature of the battery is elevated. JP-A-6-283206 (1994) and JP-A-9-45369 (1997) disclosed methods for solidifying the electrolyte by providing microcapsules, which contained a polymerization initiator and polymerizable material therein, in the electrolyte, a separator, and the like, and releasing these materials from the microcapsules to cause a polymerization reaction when the temperature of the battery was elevated.

[0006] In accordance with JP-A-6-290793 (1994), the solvent, which causes a polymerization reaction with LiPF_6 , is restricted, and mixing one of compounds in a cyclic ether group is indispensable. However, if the battery is composed of a system, wherein the use of the compound in the cyclic ether group is not desirable in view of the battery characteristics, the compound in the cyclic ether group can not be used. A result of analyzing a heat generating behavior of an electrolyte solvent made by mixing ethylene carbonate (EC) and ethylmethyl carbonate (EMC) by 1 : 1, which is one of the carbonate group solvents indicating a desirable battery characteristics with a carbon negative electrode, by a differential scanning calorimetry (DSC) indicates that the solvent alone does not indicate a large heat generation. However, a rapid reaction is indicated near 250 °C for the electrolyte dissolving LiPF_6 by one mol/liter, the carbonate solvent is decomposed, and a combustible gas is generated. As a result analyzing an infrared spectrum of the specimens after the above test, an absorption based on a carbonyl radical of the carbonate molecule was still remained at 1700 cm^{-1} with the specimen of the solvent alone. On the contrary, the absorption was disappeared with the specimen of the electrolyte dissolving LiPF_6 by one mol/liter. That means, the reaction indicated previously by the equation 1 is proceeded,

and generation of lithium carbonate and ethylene gas can be observed. Accordingly, LiPF_6 can not be used effectively as the polymerization initiator in the system using the carbonate solvent as a main solvent.

[0007] In a case when the microcapsules are used as disclosed in JP-A-6-283206 (1994) and JP-A-9-45369 (1997), the temperature whereat the polymerization initiator and polymerizable material are released can be controlled based on the material forming the wall of the capsule. However, containing a large amount of the microcapsules is difficult in view of maintaining the desirable battery characteristics. It is difficult to interrupt propagation of the thermal runaway reaction with the dispersed capsules, if the polymerization reaction does not proceed with a significant rapid reaction rate, because the reaction is generated locally with a microscale.

SUMMARY OF THE INVENTION

[0008] One of the objects of the present invention is to provide a lithium secondary battery, which is capable of terminating functions of the battery safely when any of overcharge, overdischarge, or an abnormal temperature rise occurs, without accompanying rapid change in appearance, gas generation, nor pressure change, and to provide its electrolyte and electric apparatus using the same as a power source.

[0009] The present invention is characterized in a lithium secondary battery comprising a negative electrode capable of absorbing and desorbing lithium; a positive electrode capable of absorbing and desorbing lithium; and an aprotic organic electrolyte: wherein the aprotic organic electrolyte can be solidified by a thermal reaction at a designated temperature. The aprotic organic electrolyte comprises a lithium salt and a non-aqueous solvent; the non-aqueous solvent is as much as being capable of dissolving the lithium salt, and comprises a thermally polymerizable non-aqueous solvent. Content of the non-aqueous solvent, which can dissolve the lithium salt, is in the range of 50-95 % by volume, desirably in the range of 65-90 % by volume; and content of the thermally polymerizable solvent is in the range of 5-50 % by volume, and desirably in the range of 10-35 % by volume. The aprotic organic electrolyte can be solidified by a thermal reaction at a designated temperature.

[0010] The present invention relates to a lithium secondary battery comprising a negative electrode capable of absorbing and desorbing lithium; a positive electrode capable of absorbing and desorbing lithium; and an aprotic organic electrolyte: wherein its functions can be terminated safely in a non-returned condition without accompanying rapid change in appearance, gas generation, nor pressure change, particularly pressure increase, when any of overcharge, overdischarge, or an abnormal temperature rise occurs.

[0011] The present invention also relates to an electrolyte for lithium secondary batteries; the electrolyte is characterized in comprising a lithium salt and a non-aqueous solvent, which can dissolve the lithium salt; and the electrolyte can be solidified by a thermal reaction at a designated temperature.

[0012] The present invention further relates to an electric apparatus, which is characterized in using the above described lithium secondary battery as an electric power source.

[0013] In accordance with the present invention, the electric apparatus using the lithium secondary battery as a power source can be free of protecting means such as measuring temperature and pressure of the battery against any of overcharge, overdischarge, or an abnormal temperature rise. The electric apparatus is characterized in having only a means for detecting the voltage or the current of the battery and a controlling means for switching the power source based on the above detected values; and, when any of the above abnormal condition of the secondary battery itself is caused, the functions of the battery can be terminated safely in a no reversible condition without causing a damage in appearance.

[0014] The above described electric apparatus, to which the present invention is applicable, includes such as electric vehicles, electric power storage apparatus, and so on.

[0015] In accordance with the present invention, the carbonate solvent having a superior battery characteristics can be used, and most of electrolyte is polymerized and solidified at 100 °C or higher in order to make the battery inactive and safe just before causing a degradation of the solvent by the thermal runaway with reactions with the positive electrode and the negative electrode. That is, in order to solidify the electrolyte solvent rapidly in a short time by heating, it is advantageous to maintain the reaction initiator in a condition to be dissolved in the electrolyte. In this case, the reaction initiator must be inactive with the electrolyte at room temperature, stable electrochemically in a designated range of operation voltage, and reactive with the solvent at a temperature lower than the temperature for causing reactions with the charged positive electrode and the charged negative electrode. That is, the problem can be solved by mixing a thermal reaction type solvent, which is usable in a dissolved condition, with the carbonate group solvent in the range, wherein the battery characteristics is not deteriorated.

[0010]

[0016] The above object can be achieved by making an appropriate polymerization initiator coexist at approximately 100 °C with a six membered ring carbonate, which can be polymerized by an anion polymerization, or a cation polymerization; or by making an appropriate polymerization initiator coexist with at least seven membered ring sulfite, which is known as being capable of causing a polymerization without de-sulfur dioxide. Linear diphenylcarbonate derivatives

also operate as polymerization initiators. That is, any one of diphenylcarbonate derivatives, at least six membered ring carbonate derivatives, and at least seven membered ring sulfite derivatives is used by co-dissolving with an electrolyte of the carbonate group solvent. The object can also be achieved by using the polymerization initiator in a dissolved condition.

5 [0017] As the aprotic organic electrolyte, organic solvents dissolving a lithium salt as an electrolyte and their derivatives can be used, particularly, five or less-membered cyclic compounds are desirable. That is, as the organic solvent, most of which are thermally polymerizable, but the solvents which can generate combustible gases by a thermal decomposition with adding the lithium salt are desirable; practically, such as ethylene carbonate, propylene carbonate, butylene carbonate, pentylene carbonate, hexylene carbonate, heptalene carbonate, octalene carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, dipentyl carbonate, dihexyl carbonate, diheptyl carbonate, dioctyl carbonate, methylethyl carbonate, methylpropyl carbonate, methylbutyl carbonate, methylpentyl carbonate, methylhexyl carbonate, methylheptyl carbonate, methyloctyl carbonate, ethylpropyl carbonate, ethylbutyl carbonate, ethylpentyl carbonate, ethylhexyl carbonate, ethylheptyl carbonate, ethyloctyl carbonate, propylbutyl carbonate, propylpentyl carbonate, propylhexyl carbonate, propylheptyl carbonate, propyloctyl carbonate, butylpentyl carbonate, butylhexyl carbonate, butylheptyl carbonate, butyloctyl carbonate, pentylhexyl carbonate, pentylheptyl carbonate, pentyloctyl carbonate, hexylheptyl carbonate, hexyloctyl carbonate, heptyloctyl carbonate, dioxolane, γ -butyrolactone, tetrahydrofuran, 2-methyl tetrahydrofuran, and their halogenated derivatives, and lactone derivatives, lactam derivatives, phosphoric acid ester derivatives, phosphazene derivatives, and the like.

10 [0018] As the thermal reactive solvents, or thermally polymerizable non-aqueous solvent, six or more-membered cyclic organic compounds are desirable. Practically, 6 to 10-membered cyclic carbonate such as the following compounds can be used: 1, 3-propylene carbonate, 1, 3-butylene carbonate, 1, 4-butylene carbonate, 1, 5-pentylene carbonate, 1, 6-hexylene carbonate, 1, 7-heptylene carbonate, 1, 8-octylene carbonate, and their alkyl substituted derivatives, allyl substituted derivatives, aromatic substituted derivatives, nitro substituted derivatives, amino substituted derivatives, halogen substituted derivatives, diphenyl carbonate, di(nitrophenyl) carbonate, di(methylphenyl) carbonate, di(methoxyphenyl) carbonate, di(aminophenyl) carbonate.

15 [0019] Furthermore, 7 to 11-membered cyclic sulfate compounds such as the following compounds can be used: 1, 4-butylene sulfate, 1, 5-pentylene sulfate, 1, 6-hexylene sulfate, 1, 7-heptylene sulfate, 1, 8-octylene sulfate, and their alkyl substituted derivatives, allyl substituted derivatives, aromatic substituted derivatives, nitro substituted derivatives, amino substituted derivatives, halogen substituted derivatives, and the like.

20 [0020] The thermal reactive organic solvent in the present invention can solidify the electrolyte by thermal polymerization of the organic solvent itself. However, the non-aqueous solvent itself, which can dissolve the lithium salt, can be thermally polymerized, and the whole body can be solidified.

25 [0021] The thermal reaction initiator for the non-aqueous solvent is an additive for decreasing the initiation temperature of the thermal polymerization: and practically the followings can be used: iodine, lithium iodide, lithium fluoride, lithium bromide, lithium chloride, tetrakis (4-fluorophenyl) sodium borate, tetrakis(4-fluorophenyl) lithium borate, isoazobutylnitrile, 1, 1'-azobis(cyclohexane-1-carbonitrile), 2, 2'-azobis(2-methyl-N-(1, 1-bis(hydroxymethyl)ethyl) propionamide, methyl iodide, benzene bromide, tetrabutyl ammonium iodide, trifluorodiethyl borate, triester phosphate, and others.

30 [0022] Kind and content of the reaction initiator is selected so that the polymerization and solidification reaction is initiated desirably at least 120 °C in accordance with the temperature rise by overcharge, or overdischarge, or the temperature rise based on an external environment condition. Further, the temperature is desirably at least 100 °C, and preferably at least 80 °C. Particularly, the reaction initiator, which is solidified by heating at 150 °C for 10 minutes and is not ignited in a safety test, is desirable. Therefore, as the electrolyte, a non-aqueous solvent which can be thermally polymerized at a temperature in the range of 100-150 °C is desirable. Content of the reaction initiator is desirably in the range of 0.5 - 10 % by weight to total weight of the electrolyte, and more desirably in the range of 1-5 % by weight.

35 [0023] In accordance with the present invention, at least one of current collectors of the negative electrode and the positive electrode desirably has a metallic layer such as nickel plating and the like, which is made of a harder metal than the base metal of the current collector, on a roughened surface of the current collector.

40 [0024] In accordance with the present invention, at least one of the negative electrode active material and the positive electrode active material has graphite, and the graphite is desirably composed of 20 % by weight or less of rhombohedral crystal and 80 % by weight or more of hexagonal crystal.

45 [0025] In accordance with the present invention, the lithium secondary battery comprising: a negative electrode having a negative electrode active material, which absorbs or desorbs lithium ions during a charging or a discharging period, on surface of the current collector made of a thin metallic plate; a positive electrode having a positive electrode active material on the surface of the current collector made of a thin metallic plate; and a lithium ions conductive aprotic organic electrolyte or a polymer electrolyte; is desirably treated by a process; wherein an oxide layer composed of oxide whiskers are formed on the surface of the current collector, and subsequently the oxide layer is reduced for roughening the surface; before forming the respective of the active material on the surface of the at least one of the current collector.

tors of the negative electrode and the positive electrode.

[0026] The active material is desirably formed on the surface of the current collectors composed of a thin metallic plate of at least one of the negative electrode and the positive electrode, after manufacturing the current collector to a desired thickness by cold milling and roughening the manufactured surface by the method previously described.

[0027] In accordance with the present invention, the current collector having the surface roughened by the method described previously is desirably used. That is, deterioration of the battery characteristics caused by the condition of the negative electrode current collector made of copper is mainly based on decrease in adhesiveness of the negative electrode current collector with the negative electrode active material. Therefore, the battery characteristics can be improved by increasing the adhesiveness of the current collector. Accordingly, the positive electrode current collector having as same surface as the negative electrode current collector is desirable.

[0028] The positive electrode active material and the negative electrode active material are generally desirable to be particles of 100 μm or less in diameter, the above object can be achieved by improving the adhesiveness of the particles with the materials for the current collector such as aluminum or copper.

[0029] When particles are adhered to a metal, it is effective that the surface of the metal, whereon the particles are to be adhered, is previously treated with processes; that is, a process for forming an oxide on the surface of the metal; a process for reducing a part of or whole of the above oxide by a chemical method or an electrical method; or further a process for nickel plating. The copper surface treated as above is in a roughened condition in comparison with the condition before the treatment. The surface of the copper without treating with the nickel plating does not have metallic luster of copper, but has a color of dark brown or black by optical scattering based on the roughened surface. As a method for adhering the particles onto the copper surface which has been roughened, a method comprising the steps of applying a mixture of the particles and a resin onto the roughened surface of the copper, and pressure welding and heating can be used. As another method, a method comprising the steps of applying a slurry formed by mixing the particles with a solvent dissolving a resin onto the roughened surface, and pressure welding and heating can be used. In this case, the pressure welding and the heating can be performed sequentially or concurrently, but the advantages of the present invention can be achieved similarly. The metal, of which surface has been roughened, is improved in adhesiveness with the particles, but in particular, a ratio of effective surface area to apparent surface area is desirably at least 2. For instance, in a case of a metallic foil of 100mm squares and 20 μm in thickness, the apparent surface area of the two planes is 20,000 mm^2 . When both planes of the metallic foil having the apparent surface area of S (mm^2) are treated for roughening by the above method, the apparent surface area is still remained as S (mm^2). The weight of the roughened metal foil is assumed as M (g). A specific surface area of the roughened metal foil determined by a BET method is assumed as ρ (mm^2/g). Then, the effective surface area obtained from the specific surface area is expressed by $\rho \times M$ (mm^2). Therefore, the ratio of the effective surface area/apparent surface area is expressed by $(\rho \times M)/S$ (mm^2/g).

[0030] The negative electrode current collector relating to the present invention desirably has the effective surface area of at least two times of the apparent surface area, more desirably at least three times, and preferably at least four times of the apparent surface area for obtaining a stable characteristics. The upper limit is desirably 30 times, more desirably less than 20, and preferably less than 15. The thickness of the metallic foil of the current collector is desirably in the range of 5-30 μm , and more desirably in the range of 8-20 μm .

[0031] The metallic foil of the current collector is made of aluminum for the positive electrode, and made of copper for the negative electrode. The metallic foil for surface roughening of the present invention is desirably manufactured by the steps of roughening the surface of the metallic foil as it is rolled, applying the positive active material or the negative active material onto the surface of the metallic foil in a condition of enhanced surface strength, and fabricating by pressing. Although annealing may be performed after the rolling, its surface hardness is desirably adjusted in connection with the annealing temperature with the method for fabrication by pressing.

[0032] The aprotic organic electrolyte secondary battery using the metallic foil; of which surface is treated with a method comprising at least the steps of forming an oxide on surface of the metal, reducing a part of or whole of the oxide by a chemical method or an electrical method, and further desirably performing a nickel plating; as the positive electrode current collector or the negative electrode current collector for improving the adhesiveness of the current collectors with the positive electrode active material or the negative electrode active material, has a preferable charge-discharge cycle characteristics, because falling out nor break away of the positive electrode active material or the negative electrode active material accompanied with the charge-discharge operation are scarcely generated.

[0033] In order to strengthen the surface of the base metal of the current collector, a metallic film is desirably formed on the surface of the base metal by plating after roughening the surface. The metallic film is desirably made of a metal such as cobalt, nickel, and the like, which are flexible and harder than the base metal. The metallic film is desirable in view of increasing the adhesiveness in forming the positive electrode active material and the negative electrode active material by preventing flattening at the fabrication with pressing, and increasing corrosion resistance of the surface of aluminum and copper. The thickness of the metallic film is desirably in the range of 0.01-1 μm .

[0034] The negative electrode active material can be particles, which is capable of absorbing and desorbing lithium ions, and usable materials are as follows: graphite group, amorphous carbon group, pyrocarbon group, cokes group,

carbon fiber, metallic lithium, lithium alloys (Li-Al, Li-Pb, etc.), inorganic compounds (carbide, oxide, nitride, boride, halide, intermetallic compounds, etc.), and intermetallic particle compounds such as aluminum, tin, and the like.

[0035] The above materials other than metals have desirably an average particle diameter in the range of 5-30 μm , in particular, preferably in the range of 10-20 μm . Because small particles are harmful to the characteristics, the minimum size of the particles is 5 μm or more, and the maximum size is 50 μm or less. The metallic powder is effective to increase conductivity of the film, and its average diameter is desirably in the range of 0.1-100 μm , and more desirably in the range of 1-50 μm . The graphite desirably contains rhombohedral crystal of 20 % or less by weight, and in particular, the range of 5-15 % by weight is desirable.

[0036] For positive electrode active material, a complex oxide such as, lithium cobalt oxide (Li_xCoO_2), lithium nickel oxide (Li_xNiO_2), lithium manganese oxide ($\text{Li}_x\text{Mn}_2\text{O}_4$, Li_xMnO_3), lithium nickel cobalt oxide ($\text{Li}_x\text{Ni}_y\text{Co}_{(1-y)}\text{O}_2$), and the like, is usable. The above materials have desirably an average particle diameter in the range of 5-30 μm , and in particular, the same size as the negative electrode active material other than metals is desirable.

[0037] For separator, microporous polymer resin film such as nylon, cellulose, nitrocellulose, polysulfone, polyacrylonitrile, polyvinylidene fluoride, polypropylene, polyethylene, and polyolefin group can be used.

[0038] For the electrolyte, lithium hexafluorophosphate (LiPF_6), LiBF_4 , LiClO_4 , and the like are used. Content of these materials is desirably in the range of 0.2-5 mol/l, and more desirably in the range of 0.5-3 mol/l.

[0039] For conducting material used as the negative electrode active material or the positive electrode active material, flaky graphite, massive amorphous carbon, and massive graphite are desirable. Their average particle diameter is desirably equal to or less than 10-30 μm , and the specific surface area is desirably in the range of 2-300 m^2/g , more desirably in the range of 15-280 m^2/g .

[0040] Short carbon fiber of 5-10 μm in diameter and 10-30 μm in length can be used desirably. In particular, the massive graphite has a preferable adhesiveness.

[0041] The negative electrode active material or the positive electrode active material contains a resin of 2-20 % by weight, and is combined to the surface of the current collector by the resin. For the resin, polyvinylidene fluoride is used.

[0042] The aprotic organic electrolyte secondary battery relating to the present invention has the negative electrode current collector, of which surface is appropriately roughened, and an adhesion strength of the current collector with the negative electrode mixture containing the negative electrode active material and the resin can be increased, because an anchor effect of the roughened surface of the negative electrode current collector is larger in comparison with the negative electrode current collector having a smooth surface.

[0043] Therefore, falling out and break away of the negative electrode mixture accompanied with expansion and shrinkage of the negative electrode active material during a charge-discharge operation can be prevented, and charge-discharge cycle characteristics of the aprotic organic electrolyte secondary battery can be improved.

[0044] The lithium batteries relating to the present invention can be formed in various shapes such as cylindrical shape, coin shape, rectangular shape, and the like, and are used in various portable electronic apparatus from several watt-hours to hundreds watt-hours. In particular, the lithium batteries can be used for note type personal computers, note type word processors, palm top (pocket) personal computers, portable telephones, PHSS, portable facsimiles, portable printers, headphone stereo player, video cameras, portable TVs, portable CDs, portable MDs, electric shavers, electronic note books, transceivers, electric tools, radios, taperecorders, digital cameras, portable copiers, portable game machines. And further, the lithium batteries can be used in electric vehicles, hybrid vehicles, automatic vending machines, electric carts, energy storage systems for load levelling, energy storage devices for home appliance, dispersed type energy storage systems (built in installed electric apparatus), energy supply systems for emergency, and others.

BRIEF DESCRIPTION OF THE DRAWINGS

[0045]

FIG. 1 is a cross section of the lithium secondary battery relating to the present embodiments 1 to 9,

FIG. 2 is an illustration for assembling the positive electrode, the negative electrode, and the separator of the lithium secondary battery relating to the present invention,

FIG. 3 is a graph indicating a relationship between the temperature of the specimen and calories,

FIG. 4 is a partial vertical cross section of the lithium secondary battery relating to the embodiment 10,

FIG. 5 is a vertical cross section of the coin type lithium secondary battery relating to the embodiment 11,

FIG. 6 is a vertical cross section of the rectangular type lithium secondary battery relating to the embodiment 12,

FIG. 7 is a perspective view of the assembled batteries relating to the embodiment 12,

FIG. 8 is a diagram indicating a composition of the driving system of electric vehicles relating to the embodiment 13,

FIG. 9 is a wiring diagram of the protecting circuit for the lithium secondary battery,

FIG. 10 a diagram indicating compositions of various driving control systems of the electric vehicles relating to the

embodiment 13, and

FIG. 11 is a diagram indicating a composition of the electric power storage system relating to the embodiment 14.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0046] The present invention is not restricted by the following embodiments.

(Embodiments 1-9, Comparative examples 1, 2)

[0047] FIG. 1 is a vertical cross section of the lithium secondary batteries used in the present embodiments.

[0048] In accordance with the embodiment 1, hard carbon was used as a negative electrode active material layer 5, polyvinylidene fluoride (hereinafter, called as PVDF) was used as a binder; and a negative electrode was obtained by applying a paste made by dissolving the above materials into N-methylpyrrolidone (hereinafter, called as NMP) onto both sides of a copper foil negative electrode current collector 6 of 20 μm thick, heating, and pressing for fabrication. LiMn_2O_4 was used as a positive electrode active material 7, PVDF was used as a binder, amorphous carbon was used as a conductive assistant agent; and a positive electrode was obtained by applying a paste made by dissolving the above materials into NMP onto both sides of an aluminum foil positive electrode current collector 8 of 20 μm thick, heating, and pressing for fabrication. A battery of 54 mm in outer diameter and 200 mm in height was prepared by; fixing tabs for taking out current 16, 17, at an end of these positive electrode and the negative electrode by welding with an equal interval; winding these electrodes with separators 9, each of which was interposed in each of intervals between these electrodes as indicated in FIG. 2; connecting the tabs with a battery lid 15 having electrode terminals 10, 11; inserting the battery lid into the battery can 14; injecting an electrolyte into the battery; and fixing the battery lid 15 to the battery can 14 by caulking. In accordance with the embodiment 1, the electrolyte was prepared by dissolving LiBF_4 by 1 mol/l as a lithium salt into a solution, which was prepared by mixing propylene carbonate (hereinafter, called PC) with ethylmethyl carbonate (hereinafter, called EMC) and 1, 3-propylene carbonate by 60:30:10 by volume; and further dissolving iodine by 5 % by weight into the solution, as indicated in Table 1. The amount of the electrolyte injected into the battery was approximately 85 ml.

[0049] Similarly, the batteries of the embodiment 2-9 and the comparative examples 1, 2 were prepared as indicated in Table 1.

[0050] The battery characteristics of the batteries prepared as above were evaluated by measuring a first discharge capacity with a passing current of 10 A, and a discharge capacity after continuously repeated charge-discharge cycle tests of 300 times with setting a discharge utilizing rate as 70 %. As safety tests, heating tests by burner with a gas furnace were performed, because a large battery had a large amount of electrolyte and a danger to be thrown into fire was deemed as the highest danger. The results of the above evaluation and tests are summarized in Table 1.

Table 1

Emb./Com. ¹⁾	Electrolyte	Electrolyte/additive
Emb. 1	PC:EMC:1,3-propylene carbonate = 60:30:10	LiBF ₄ = 1 M, Iodine = 5 wt. % ²⁾
Emb. 2	PC:EMC:1,3-propylene carbonate = 60:30:10	LiPF ₆ = 1 M, Iodine = 5 wt. %
Emb. 3	PC:EMC:1,3-propylene carbonate = 60:30:10	LiPF ₆ = 1 M, Lithium iodide = 2 wt. %
Emb. 4	PC:EMC:1,3-propylene carbonate = 60:30:10	LiBF ₄ = 1 M, Triphenyl phosphate = 5 wt. %
Emb. 5	PC:EMC:diphenyl carbonate = 60:30:10	LiBF ₄ = 1 M
Emb. 6	PC:EMC:diphenyl carbonate = 60:30:10	LiPF ₆ = 1 M
Emb. 7	PC:EMC:1,4-butylene sulfate = 60:35:5	LiBF ₄ = 1 M
Emb. 8	PC:EMC:1,4-butylene sulfate = 60:35:5	LiPF ₆ = 1 M
Emb. 9	EMC:1,3-propylene carbonate = 65:35 sulfate = 60:35:5	LiPF ₆ = 1 M Iodine = 2 wt. %
Com. 1	PC:EMC = 60:30	LiPF ₆ = 1 M
Com. 2	PC:EMC = 60:30	LiBF ₄ = 1 M

Remarks:

1) Emb./Com.: Embodiment/Comparative example

2) wt. % : % by weight

Table 1(continued)

Emb./Com. ¹⁾	First discharge capacity (Ah)	300th discharge capacity (Ah)	Results of burner tests.
Emb. 1	19.5	16.8	No ignition
Emb. 2	19.6	16.4	No ignition
Emb. 3	19.5	16.3	No ignition
Emb. 4	19.6	16.3	No ignition
Emb. 5	19.4	16.5	No ignition
Emb. 6	19.6	16.6	No ignition
Emb. 7	19.4	16.4	No ignition
Emb. 8	19.5	16.3	No ignition
Emb. 9	19.6	16.7	No ignition
Com. 1	19.6	16.7	Ignition
Com. 2	19.4	16.6	Ignition

1) Emb./Com.: Embodiment/Comparative example

[0051] As indicated in Table 1, the electrolyte burst forth from the batteries of the comparative examples 1 and 2, wherein conventional electrolyte was used, after 4-5 minutes after igniting the burner in the furnace, and caused combustion by catching fire from the flame in the burner. The combustion continued approximately 20 minutes. On the contrary, the electrolyte of the batteries obtained in the embodiments 1 - 9, wherein the electrolyte having a thermal self solidifying effect of the present invention was used, were all solidified and did not indicate any ignition of the electrolyte.

[0052] Conductivity of the electrolyte of the embodiment 9 was 9 mS/cm. Reactivity of the electrolyte was evaluated by a differential scanning calorimetry (DSC). The result is indicated in FIG. 2. The electrolyte initiated its reaction at approximately 140 °C, and heat was generated. The specimen after the test was solidified. Therefore, the electrolyte was confirmed to be solidified at approximately 140 °C.

(Embodiment 10)

[0053] The lithium secondary battery of the present invention indicated in FIG. 4 was prepared similarly as follows: a slurry of a positive electrode mixture was prepared by mixing LiCoO₂ as the positive electrode active material, acetylene black of 7 % by weight as a conductor, polyvinylidene fluoride (PVDF) of 5 % by weight as a hinder, and N-methyl-2-pyrrolidone.

[0054] Similarly, a slurry of a negative electrode mixture was prepared by mixing graphite powder having an arbitrary content of rhombohedral crystalline in the range of 5-20% by weight and hexagonal crystalline of at least 80 % by weight as the negative electrode active material, PVDF of 10 % by weight as a binder, and N-methyl-2-pyrrolidone. The graphite powder had an average particle diameter of 25 μm, and the amount of the rhombohedral crystalline was

adjusted by varying heating time at 2850 °C.

[0055] The positive electrode mixture was applied onto both side planes of an aluminum foil of 25 µm in thickness, and then, dried in vacuum at 120 °C for one hour. After drying in the vacuum, the electrode was fabricated by pressing with a roller press to make the electrode 195 µm in thickness. The amount of the applied mixture per unit area was 55 mg/cm², and the positive electrode was prepared by cutting out the electrode to 40 mm in width and 285 mm in length. However, the regions in 10 mm from both ends of the positive electrode were not applied with the positive electrode mixture and the aluminum foil was exposed, and a positive electrode tab was fixed onto one of these end regions by an ultrasonic welding.

[0056] On the other hand, the negative electrode mixture was applied onto both side planes of a copper foil of 10 µm in thickness, which was as rolled and treated by a reducing process after oxidation treatment as explained later, and then, dried in vacuum at 120 °C for one hour. After drying in the vacuum, the electrode was fabricated by pressing with a roller press to make the electrode 175 µm in thickness. The amount of the applied mixture per unit area was 25 mg/cm², and the negative electrode was prepared by cutting out the electrode to 40 mm in width and 290 mm in length. The regions in 10 mm from both ends of the positive electrode were not applied with the negative electrode mixture as well as the positive electrode, and the copper foil was exposed, and a negative electrode tab was fixed onto one of these end regions by an ultrasonic welding.

[0057] For the separator, a microporous film made of polypropylene of 25 µm in thickness and 44 mm in width was used.

[0058] The positive electrode, the separator, and the negative electrode were overlapped in the order as described above, and an electrode group was prepared by winding the overlapped members as indicated in FIG. 2. The electrode group was inserted into a battery can, the negative electrode tab was welded to the bottom of the battery can, and a reduced area portion was formed in order to caulk a positive electrode lid. After pouring an electrolyte; the electrolyte was prepared by mixing lithium phosphate hexafluoride by 1 mol/l with a mixed solvent of ethylene carbonate, diethylcarbonate, and 1, 3-propylene carbonate of 45:45:10 by volume, and further mixing iodine of 2 % by weight to the total amount of the electrolyte; into the battery can, a positive electrode tab was welded to the positive electrode lid, and a battery was assembled by caulking the positive electrode lid to the battery can. The battery can 14 was made of austenitic stainless steel such as SUS 304, and SUS 316.

[0059] Using the prepared battery, charge-discharge cycles were repeated with charge-discharge current of 300 A, and charge-discharge voltages of 4.2V and 2.8V, respectively. A rapid charge-discharge was performed with varying the charging current in the range from 300 mA to 900 mA.

[0060] Copper plates as rolled were used for the following tests in a condition of a tough pitch copper of 0.1 mm in thickness and 100 mm squares in width. The surface of the copper plate was treated by an oxidation process, and subsequently a reducing process.

[0061] The copper plate was degreased with the following condition and, subsequently, washed with water.

C4000	50 g/l
liquid temperature	55 °C

[0062] Then, the copper plate was treated with a following mixture, and subsequently, washed with water.

ammonium disulfate [(NH ₄) ₂ S ₂ O ₄]	200 g/l
sulfuric acid (H ₂ SO ₄)	5 ml/l
liquid temperature	30 °C

[0063] Then, the copper plate was washed with the following acid, and subsequently washed with water.

sulfuric acid (H ₂ SO ₄)	3 ml/l
---	--------

[0064] Then, the copper plate was treated with a following mixture for oxidation treatment to deposit copper oxide onto the copper plate surface.

sodium chlorate (NaCl_3O)	109 g/l
sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$)	30 g/l
sodium hydroxide (NaOH)	15 g/l
liquid temperature	75 °C

[0065] After washing with water, the copper plate was treated with a following mixture for reducing treatment.

dimethylamine borane [$(\text{CH}_3)_2\text{NHBH}_3$]	6 g/l
sodium hydroxide (NaOH)	5 g/l
liquid temperature	45 °C

[0066] Then, the copper plate was washed with pure water, and dried with hot blowing. Each of the above treatment was performed by immersing into the agitated solution at a designated time.

[0067] The C4000 is an agent for cleaning the surface of the copper plate after rolling, further, sodium hydroxide is added in order to make the pH of the solution in the range of 11-13, and a surface active agent is also added. The ammonium disulfate is added for dissolving the surface of the copper plate, and the sulfuric acid is added for dissolving copper oxide.

[0068] The treated surface conditions could be controlled by time, temperature, and concentration of the solution for the oxidation treatment, and various specimens were prepared by varying the treating time. The treating time were 60 seconds, 120 seconds, and 300 seconds. The surface of the copper plate after the treatment was observed with a scanning electron microscope, and a fact that the surface of the copper plate became coarser in accordance with extending the oxidation treating time was confirmed from the result of the observation. Effective surface area was obtained by measuring the specific surface area by a BET method using Kr gas. Ratios of the effective surface area to the apparent surface area of the copper plate are indicated in Table 2.

Table 2

No.	Oxidation treating time (sec.)	Effective surface area/apparent surface area
1	0	0.7
2	60	3.3
3	120	6.5
4	300	12.4

[0069] The No. 1 is a blank sample using the copper plate as rolled without performing any treatment thereon.

[0070] Table 2 indicates that the surface roughening of the copper plate is proceeded with extending the oxidation treating time. The blank test No. 1 indicates a ratio of effective surface area/apparent surface area of less than 1, because of an experimental error in measuring the specific surface area by the BET method. Accordingly, each of the above ratios shown in Table 2 can be deemed as containing an error as much as the No. 1.

[0071] The effective surface area is increased approximately linearly with increasing the oxidation treating time, and the ratio of the effective surface area becomes three times or more in one minute and the ratio indicates a trend to increase more gradually after 200 seconds.

[0072] In accordance with the present embodiment, the surface of the copper plate after oxidation treatment for 300

seconds was observed with an electron microscope, and formation of whisker oxide of 1-30 nm in diameter and 50-200 nm in length was confirmed. In accordance with subsequent reducing treatment, rods of 100-500 nm in length were formed and stood with intertwining rod shaped coating film of 5-20 nm in diameter each other on the surface of the whisker oxide. The diameter and the length of the rods vary depending on the length of the treating time.

[0073] Then, adhesiveness of the copper plate with the particles is explained hereinafter.

[0074] As the particles, flaky graphite having an average diameter of approximately 25 μm , massive amorphous carbon having an average diameter of approximately 15 μm , and aluminum powder having an average diameter of approximately 30 μm were used. A slurry was prepared by kneading each of the particles with N-methylpyrrolidone solution dissolving polyfluorovinylidene (PVDF). The slurry was applied onto the copper plate indicated in Table 2. The ratio of each of the particles to the PVDF in the slurry was particles:PVDF = 90:10 by weight. The copper plate applied with the slurry was dried in atmosphere, pressed with a pressure of 500 kg/cm² in order to increase the density of the film, and dried in vacuum at 120 °C. The particles adhered copper plate prepared by the above steps was cut out to make the particles adhered surface area 4 cm², and commercial adhesive tape was adhered so as to cover all the particles adhered surface of the copper plate. The adhesiveness of the copper plate with the particles was evaluated by the ratio of the separated particles when the adhesive tape is peeled off from the surface of the copper plate. The result is indicated in Table 3.

Table 3

No.	Ratio of separated particles when peeling off the adhesive tape from the copper plate (% by weight)		
	Flaky graphite	Massive amorphous carbon	Aluminum
1	75	99	99
2	28	35	13
3	34	17	15
4	34	19	13

[0075] In accordance with Table 3, the smaller the ratio of separated particles is when peeling off the adhesive tape from the surface of the copper plate, the better the adhesiveness of the copper plate with the particles is. Accordingly, the copper plate, of which surface was roughened by treating with the oxidation process and the reducing process, had a better adhesiveness than the copper plate as rolled. Although the adhesiveness varies depending on the kind and size of the particles, the adhesiveness of the surface roughened copper plate was clearly improved in comparison with the copper plate as rolled.

[0076] That is, in the relationship between the ratio of the separated particles and the ratio of effective surface area/apparent surface area, the ratios of the separated particles of the flaky graphite and aluminum powder were saturated when the ratio of effective surface area/apparent surface area was 2 or more, and the values were decreased to 35 % or less for the former and of 15 % or less for the latter.

(Embodiment 11)

[0077] FIG. 5 is a cross sectional view of a coin type battery relating to the present invention. The current collectors used for the positive electrode and the negative electrode, and the positive electrode mixture and the negative electrode mixture of the present embodiment were prepared as same as the embodiment 10. The negative electrode was a pellet of 14.5 mm in diameter, and 0.4 mm in thickness. The positive electrode was a pellet of 14.5 mm in diameter, and 0.9 mm in thickness. As indicated in FIG. 5, the positive current collector was fixed to inner bottom of the positive electrode can by welding, a gasket made of insulating packing was placed thereon, and the positive electrode was pressure welded to the positive electrode can. A separator made of microporous polypropylene was placed thereunder, and an electrolyte was impregnated into the separator. The electrolyte was prepared by dissolving LiPF₆ of 1 mol/l into a mixed solvent of ethylene carbonate, propylene carbonate, diethylcarbonate, and 1, 3-propylene carbonate of 30:15:45:10 by volume, and further dissolving iodine of 2 % by weight to total weight of the solution into the solution. On the other hand, a negative electrode current collector was welded to inner plane of the negative electrode can 4, and the negative electrode was pressure welded to the negative electrode current collector. Then, the negative electrode was placed on the separator, and the positive electrode can and the negative electrode can were caulked together via the gasket to form the coin type battery.

(Embodiment 12)

[0078] The positive electrode active material used in the present embodiment was LiCoO_2 powder having an average particle diameter of 10 μm . A positive electrode slurry was prepared by kneading sufficiently the above positive electrode active material, natural graphite, and 1-methyl-2-pyrrolidone solution of polyfluorovinylidene. The mixing ratio of LiCoO_2 :natural graphite: polyfluorovinylidene was 90:6:4 by weight. The slurry was applied onto the positive electrode current collector made of aluminum foil of 20 μm in thickness by a doctor blade method. The positive electrode was a rectangular shape of 70 mm in height and 120 mm in width. The positive electrode was dried at 100 °C for 2 hours.

[0079] The negative electrode was manufactured as follows. The negative electrode slurry was prepared by mixing natural graphite powder having an average particle diameter of 5 μm with polyfluorovinylidene in 90:10 by weight, and kneading the mixture with 1-methyl-2-pyrrolidone added as an organic solvent. The slurry was applied onto surface of the negative electrode current collector made of copper foil of 10 μm in thickness as rolled by a doctor blade method. The surface of the copper foil was treated by the same condition as the embodiment 4. The negative electrode was a rectangular shape of 70 mm in height and 120 mm in width. The negative electrode was dried at 100 °C for 2 hours.

[0080] FIG. 6 is a cross sectional view of the rectangular type lithium secondary battery of the present invention. the outer size of the battery was 100 mm in height, 130 mm in width, and 30 mm in depth. An electrode group was formed by laminating alternately the positive electrodes 31 and the negative electrodes 32, each of which was inserted into a separator 33 manufactured in a bag shape, and inserted into a battery can 34 made of aluminum. Each of the positive electrode lead 35 and the negative electrode lead 37 welded to an upper portion of each electrode was connected to each of the positive electrode terminal 38 and the negative electrode terminal 39, respectively. Each of the positive electrode terminal 38 and the negative electrode terminal 39 was inserted into a battery lid 41 via a packing 40 made of polypropylene. The battery can be connected with external cables by nuts 20 attached to the positive electrode terminal 38 and the negative electrode terminal 39. The battery lid 41 was provided with a safety valve for releasing gases accumulated inside the battery when pressure of inside the battery reached 4-7 atmosphere, and an electrolyte inlet. The safety valve comprises a gas release outlet 42, an o-ring 43, and a sealing bolt 44. The electrolyte inlet comprises a pouring hole 45, an o-ring 46, and a sealing bolt 47. After welding the battery can 34 and the battery lid 41 by laser, the electrolyte was poured into the battery through the pouring hole 45, and the pouring hole 45 was sealed by the sealing bolt 47 to complete the lithium secondary battery. The electrolyte used was a mixed solvent 1 liter of ethylene carbonate, dimethyl carbonate, and 1, 3-propylene carbonate of 45:45:10 by volume dissolving lithium phosphate hexafluoride (LiPF_6) 1 mol and iodine 5 % by weight.

[0081] Electrochemical energy of the battery can be taken out and rechargeable through the positive electrode terminal 38 and the negative electrode terminal 39. An average discharge voltage of the battery is 3.7 V, and rated capacity is 27 Ah, and 100Wh.

[0082] A battery assembly of 8 batteries connected in series indicated in FIG. 7 was assembled by aligning the above rectangular lithium secondary batteries 21 in a row so that their side plane of 100 mm in height and 130 mm in width y were faced each other and their lids 11 were oriented upwards.

[0083] In accordance with the present invention, the thickness of the spacer was restricted to less than 10 % of the battery thickness, in order to maintain a decreasing rate of the volume energy density of the battery assembly by using the spacer approximately 10 %. Because the battery 21 had a thickness of 30 mm, two spacers 22 made of polytetrafluoroethylene of 10 mm in thickness, 10 mm in width, and 100 mm in length were inserted in each of intervals between the facing planes of the batteries in a direction along the height of the battery 21. The rectangular lithium secondary battery 21 was tightened so as to be pressurized inwards by fixing metallic plates made of stainless steel 23 and fixing members 28 made of polytetrafluoroethylene attached at side planes, front plane, and rear plane of the battery assembly with bolts 29. In order to release heat from the battery outwards rapidly, rib shaped protrusion was formed on the metallic plate 23 made of stainless steel. The positive electrode terminals and the negative electrode terminals of each rectangular lithium secondary batteries were connected with current cables so that all the batteries are connected in series, and further connected to the positive electrode terminal 24 and the negative electrode terminal 25 of the battery assembly. Furthermore, the positive electrode terminal and the negative electrode terminal of each of the batteries 21 were connected to a control circuit board 26 with the positive electrode voltage input cable and the negative electrode voltage input cable, respectively, in order to measure voltage and current of each battery 21 for controlling charge-discharge of the battery assembly. The control circuit board 26 was provided with microcomputer chips, and had a function to terminate charge-discharge of the battery assembly when any one of the voltage and the current of at least one of the batteries 21 went out a designated range. The control circuit board of the present invention was a flame retardant board improved in safety, because circuit elements were connected using printed circuit board made of epoxy resin added with glass fiber and hexabromobenzene 1 %, and wiring cable coated with polytetrafluoroethylene. A thermocouple 43 was attached to the side plane of the fourth battery from the battery at the end of the row for transmitting a temperature signal to the control circuit board 26, in order to terminate the charge-discharge of the battery when temperature of the battery exceeded a setting temperature. In accordance with the present embodiment, the control cir-

cuit board 26 was provided on the battery assembly. Therefore, a shielding plate 27 was inserted between the control circuit board 26 and the battery 21, in order to prevent the electrolyte released from the gas release outlet 42 from contaminating the control circuit board 26. An average discharge voltage of the battery assembly is 29.6 V, and the rated capacity is 27 Ah, and 800Wh. The battery assembly of the present embodiment is expressed as B1, hereinafter.

Because the battery assembly of the present invention does not require any external vessel, the rectangular lithium secondary battery 21 can be cooled directly with outside air, and a temperature rise of the battery at rapid charge or discharge under a high loading can be decreased.

[0084] In accordance with the above explanation, the electrode group was a laminated type using rectangular shaped electrodes. However, the similar battery assembly can be composed with a wound type electrode group using flat and oblong shaped electrodes.

(Embodiment 13)

[0085] FIG. 8 is a diagram indicating a composition of the driving system of electric vehicles using the lithium secondary batteries described in the above embodiments 1-12.

[0086] In accordance with the driving system of the electric vehicle of the present embodiment, when a key switch is turned on and depressing the accelerator, torque or rotation of motor can be controlled corresponding to a depressing angle of the accelerator, as same as ordinary gasoline cars. When the accelerator is returned to its original location, a regenerative brake equivalent to an engine brake is started to operate, and when brake pedal is depressed deeply, the regenerative brake force is increased further. Switching of going forward or backward is performed by shift lever signal, and transmission gear ratio is set at all times a fixed value. An IGBT vector control inverter system using an induction motor was adopted as a control system, and power source voltage was selected as 336 V in consideration of the IGBT withstand voltage. In accordance with the present embodiment, output was determined as the maximum output 45 kW, the maximum torque 176 N.m in consideration of dynamic performance (acceleration, grade ability) of the vehicle, and rated output was determined as 30 kW in consideration of specification of the maximum velocity. Main control items included a fail safe control, in addition to controlling the going forward and backward of the vehicle, and regenerative brake.

[0087] In accordance with decreasing size and weight of motors, thermal density is increased. Therefore, making effective cooling structures becomes important. If an ordinary air cooling type is adopted, the temperature of the motors would be increased. Therefore, a liquid cooling type as same as general engines was adopted. Coolant paths were provided in frame, made of aluminum, covering a body of the motor itself, and an optimum shape was determined by temperature rise simulation. The coolant entered into the coolant paths through an inlet of the coolant at the frame, released from the frame after absorbing the heat generated at the motor itself, and cooled by the radiator in the circulating paths of the coolant. In accordance with the liquid cooling structure as described above, the cooling performance could be increased approximately three times in comparison with air cooling structure.

[0088] IGBT are used as power elements in the inverter, and heat as several kW at maximum is generated with the maximum output. Additionally, heat is generated from resistance for absorbing surge, filter condenser, and others. Therefore, effective cooling to maintain these members lower than allowable temperature is necessary. Particularly, cooling of the IGBT is a problem, and air-cooling, water cooling, oil cooling, and other cooling system can be considered. Here, a forced water cooling system, which was readily operable and available of effective cooling, was adopted.

[0089] A protection circuit indicated in FIG. 9 is composed for the lithium secondary battery as a power source in the present embodiment. The protection circuit is to protect the battery from over-charging and over-discharging. The protection circuit is composed of balance compensation circuits for adjusting cell voltage of respective battery as indicated in FIG. 9, and provided to each of the batteries. The balance compensation circuit can be controlled by a microcomputer. Because the electrolyte of conventional lithium secondary battery was flammable, thermister was provided to each of the batteries for monitoring the batteries by detecting temperature or pressure. However, in accordance with the present embodiment, any special monitoring of temperature or pressure is made unnecessary, because the electrolyte of the present embodiment does not have any flash point before solidifying itself when an igniting source is approached closely to the electrolyte. Therefore, safety devices as protection circuits could be decreased. The power source is automatically switched off when any of overdischarge or overcharge is detected as shown in FIG. 8.

[0090] In accordance with the present embodiment, an example using an induction motor is indicated. However, the present invention can be applied additionally to electric vehicles using permanent magnet type synchronous motor, and DC shunt motor similarly as shown in FIG. 10. In FIG. 10, each of abbreviations expresses followings: INV (inverter), IM (induction motor), E (encoder), SM (synchronous motor), PS (position sensor), PWM (pulse width modulation), DCM (DC motor), CH (chopper), N⁺ (velocity instruction), and T⁺ (torque instruction). In accordance with FIG. 10, each of columns indicates controlling system, system composition, and main controlling parameters.

(Embodiment 14)

[0091] FIG. 11 is a wiring diagram indicating a composition of electric power storage system for night electric power using any of the lithium secondary batteries described in embodiments 1 to 12. The present example of the electric power storage system is 2000 kW x 4 h, cell capacity is 1000 Wh. The present example indicates 360 batteries connected in series, and connected 24 rows in parallel. In accordance with the present embodiment, the batteries must be protected from the overdischarge or overcharge as same as the embodiment 13, and the protection circuit indicated in FIG. 9 is used as the circuit for monitoring and balance compensation, in order to protect the batteries as well as the previous embodiments.

[0092] The present embodiment is aimed at storing a large capacity of electric power, but the present embodiment is also effective for air conditioners and electric water heater for home.

[0093] In accordance with the present invention, safety when the battery is thrown into fire, it is one of serious concerns for the large scale lithium secondary battery, can be improved significantly, and significant advantages of obtaining large scale lithium secondary batteries having high safety for home electric power storage and for electric vehicles can be achieved.

Claims

1. A lithium secondary battery comprising :

a negative electrode (5, 6), which is capable of absorbing and desorbing lithium,
a positive electrode (7, 8), which is capable of absorbing and desorbing lithium, and
a non-aqueous electrolyte, wherein
said non-aqueous electrolyte is solidified by a thermal reaction at a designated temperature.

2. A lithium secondary battery as claimed in claim 1, wherein

said non-aqueous electrolyte is composed of:
at least a lithium salt and a non-aqueous solvent, and,
said non-aqueous solvent comprises:
a non-aqueous solvent which can dissolve said lithium salt, and
a thermally polymerizable non-aqueous solvent.

3. A Lithium secondary battery as claimed in claim 2, wherein

said thermally polymerizable non-aqueous solvent is composed by dissolving at least one of cyclic carbonate derivatives having a six to ten membered ring.

4. A Lithium secondary battery as claimed in claim 2, wherein

said thermally polymerizable non-aqueous solvent is composed by dissolving at least one of diphenyl carbonate derivatives.

5. A Lithium secondary battery as claimed in claim 2, wherein

said thermally polymerizable non-aqueous solvent is composed by dissolving at least one of sulfate derivatives having a seven to eleven membered ring.

6. A lithium secondary battery as claimed in any one of claims from 1 to 5, wherein

said non-aqueous electrolyte in any one of claims from 1 to 5 is composed by dissolving at least one of iodine, lithium iodide, lithium fluoride, lithium bromide, lithium chloride, tetrakis(4-fluorophenyl)sodium borate, tetrakis(4-fluorophenyl) lithium borate, isoazobutylnitrile, 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis(2-methyl-N-(1,1-bis(hydroxymethyl)ethyl) propionamide, methyl iodide, bromobenzene, tetrabutylammonium iodide, trifluorodiethyl borate, and triester phosphate, as an initiator for the thermal reaction.

7. A lithium secondary battery as claimed in any one of claims from 1 to 6, wherein

said non-aqueous electrolyte contains at least 70 % by volume of an ester carbonate solvent therein.

8. A lithium secondary battery comprising :

a negative electrode (5, 6), which is capable of absorbing and desorbing lithium,
a positive electrode (7, 8), which is capable of absorbing and desorbing lithium, and
a non-aqueous electrolyte,
which stops its operation in a non-reversible condition without showing any significant change in appearance
when any of overcharge, overdischarge or abnormal temperature rise occurs.

9. A lithium secondary battery comprising :

a negative electrode (5, 6), which is capable of absorbing and desorbing lithium,
a positive electrode (7, 8), which is capable of absorbing and desorbing lithium, and
a non-aqueous electrolyte,
which stops its operation in a non-reversible condition without generating gases rapidly in said battery when
any of overcharge, overdischarge or abnormal temperature rise occurs.

10. A lithium secondary battery comprising :

a negative electrode (5, 6), which is capable of absorbing and desorbing lithium,
a positive electrode (7, 8), which is capable of absorbing and desorbing lithium, and
a non-aqueous electrolyte,
which stops its operation in a non-reversible condition without showing a rapid pressure change in said battery
when any of overcharge, overdischarge or abnormal temperature rise occurs.

11. An electrolyte for lithium secondary batteries comprising:

at least a lithium salt, and
a non-aqueous solvent which can dissolve said lithium salt,
which can be solidified by a thermal reaction at a designated temperature.

12. Electric apparatus using a lithium secondary battery as claimed in any one of claims from 1 to 10.

13. Electric apparatus using a lithium secondary battery as a power source,

which is free from monitoring temperature and pressure of said battery as protection means against over-
charge, overdischarge, or abnormal temperature rise of said battery;
which comprises means for detecting voltage or current of said battery, and a controlling means for switching
said power source in accordance with a detected value by said means for detecting voltage or current of said
battery; and
which stops its operation in a non-reversible condition without showing any significant damage in appearance
when any of overcharge, overdischarge or abnormal temperature rise occurs in the secondary battery itself.

14. Electric apparatus as claimed in any of claims 12 and 13,

which is used for any of electric vehicles and electric power storage apparatus.

FIG. 1

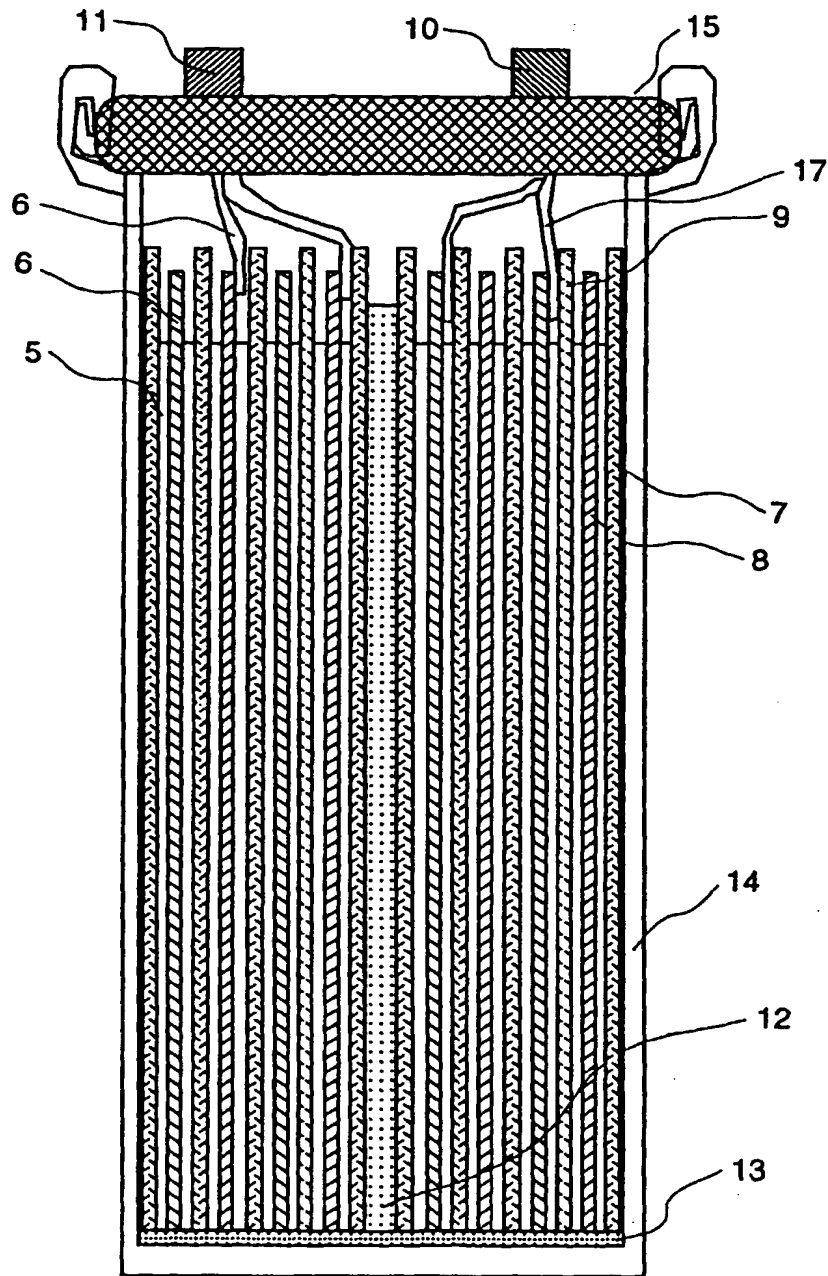


FIG.2

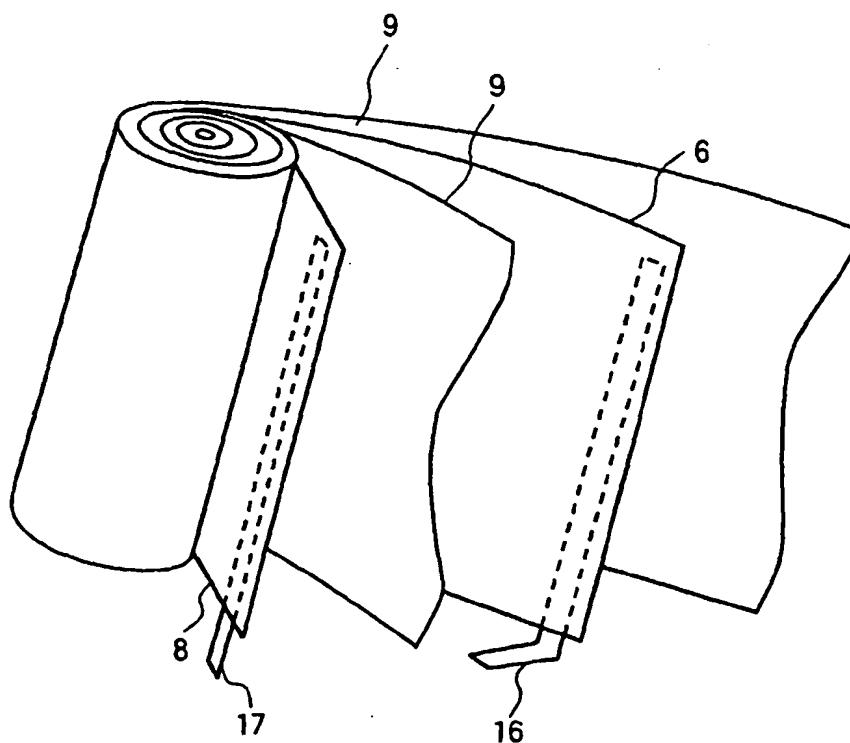


FIG.3

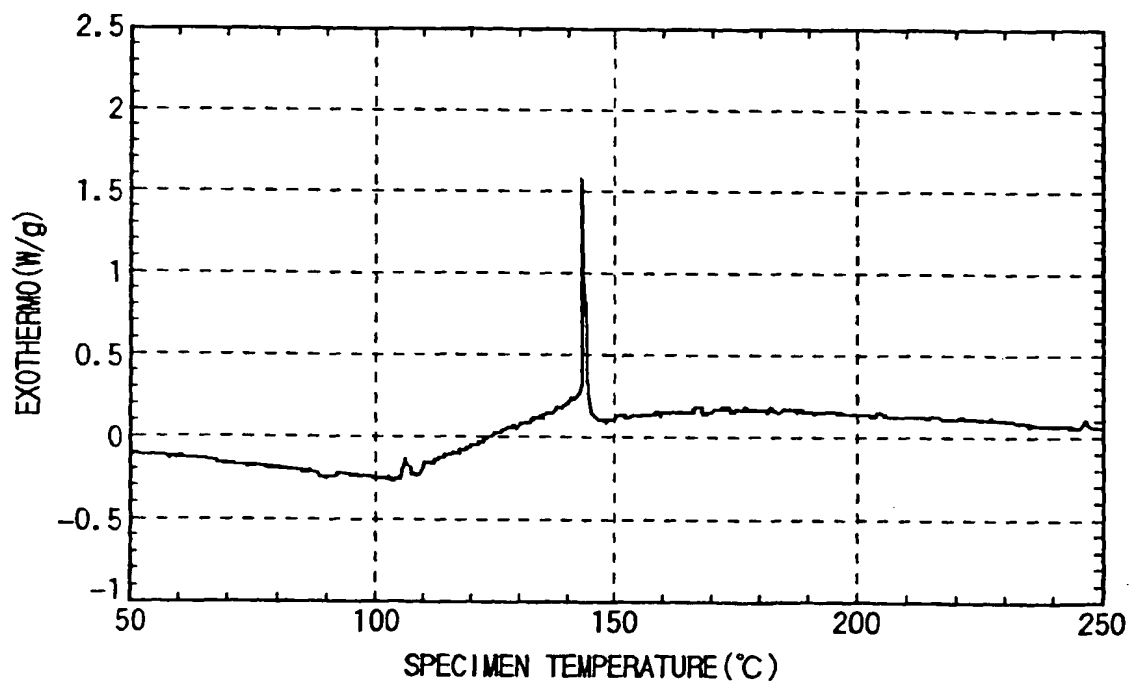


FIG.4

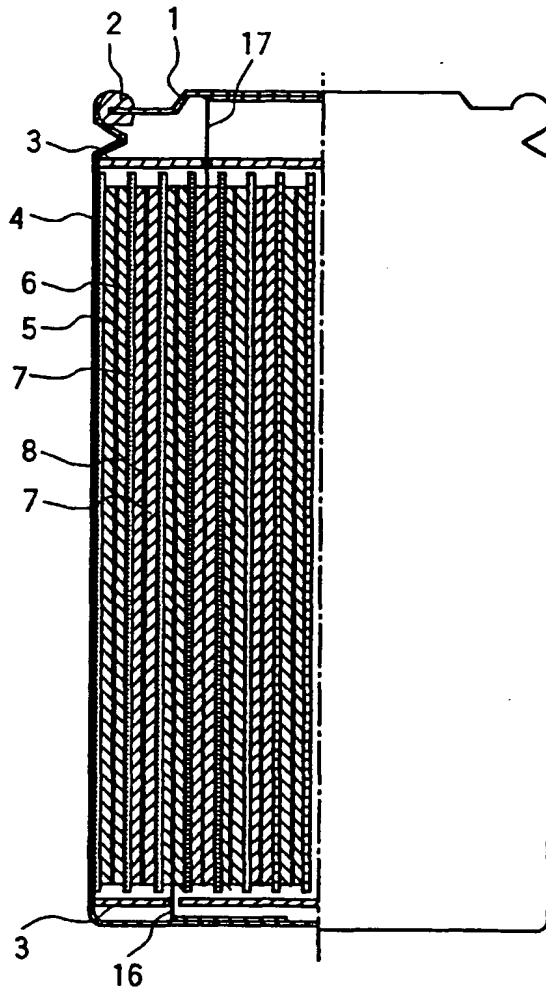


FIG.7

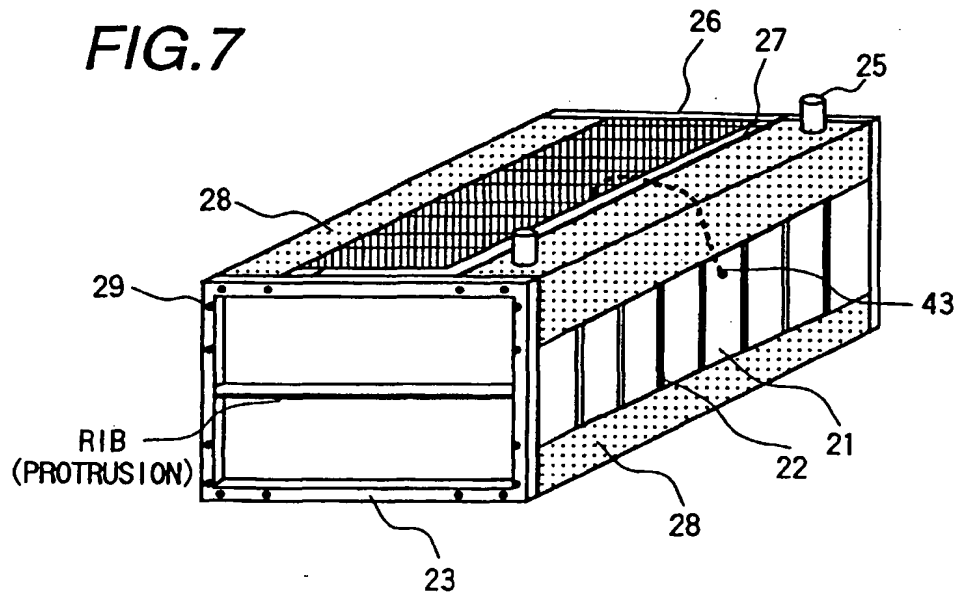


FIG.5

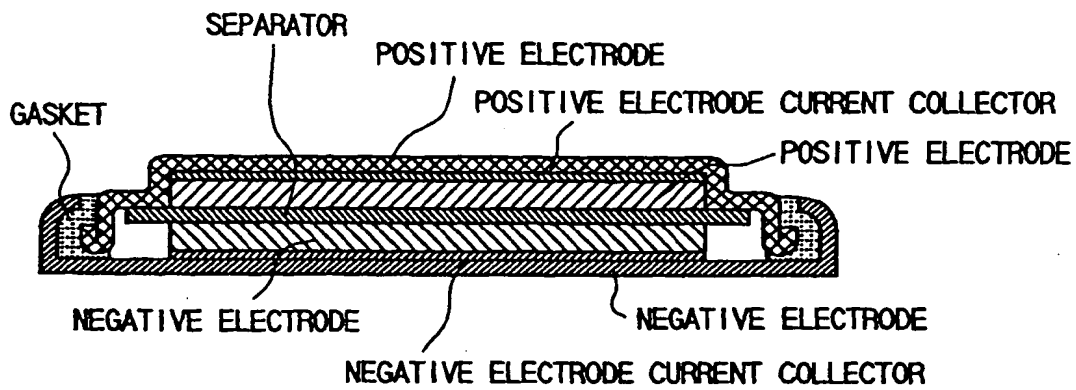


FIG.6

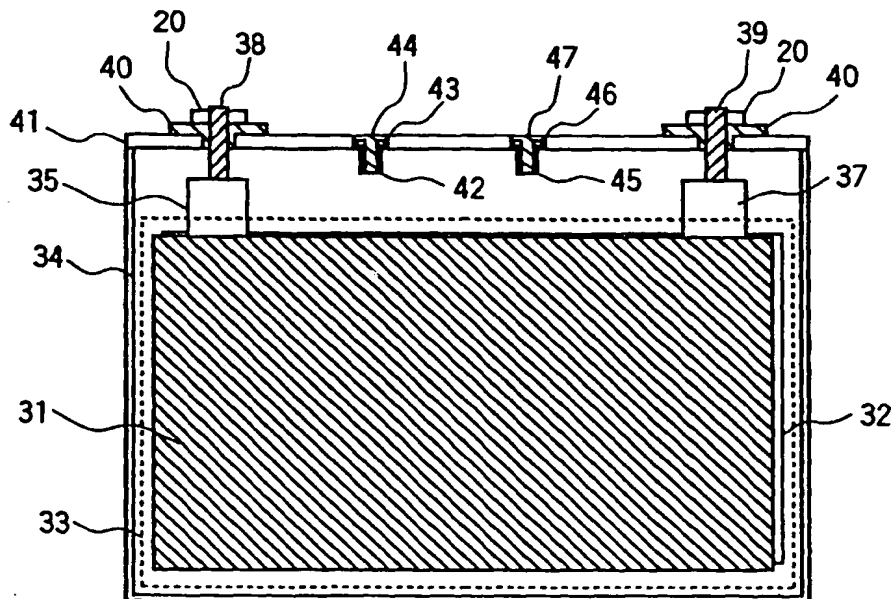


FIG.8

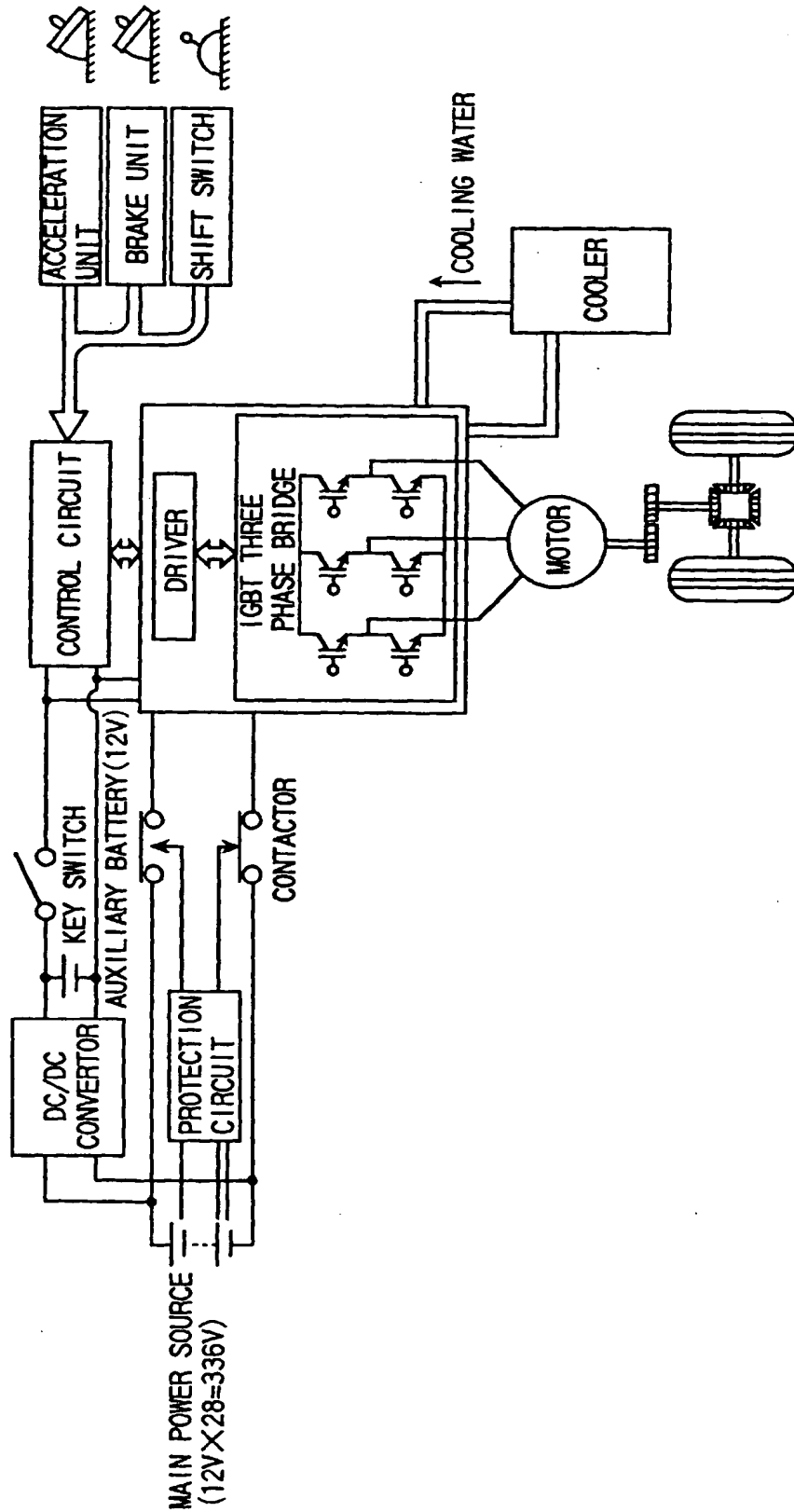


FIG.9

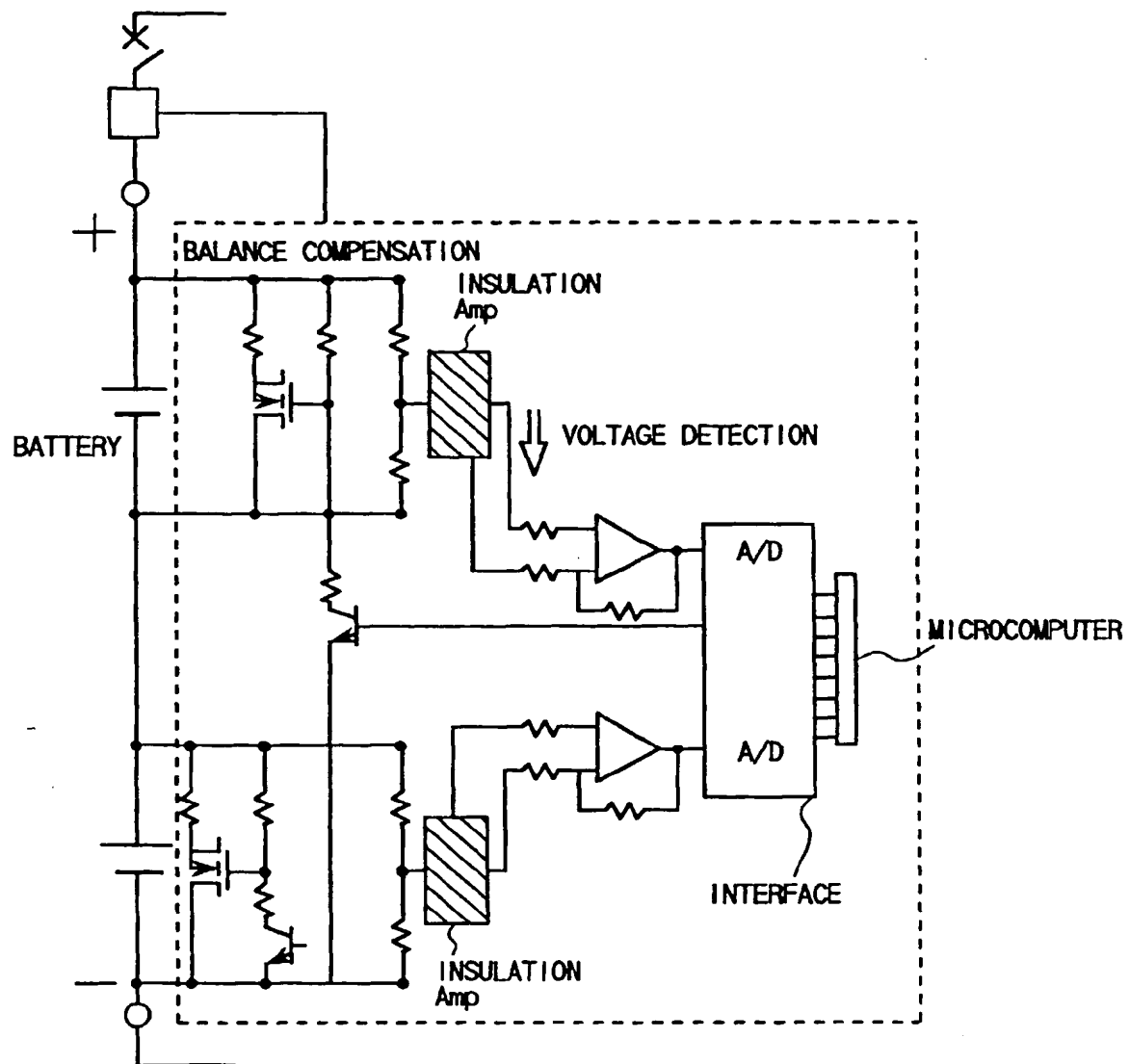


FIG.10

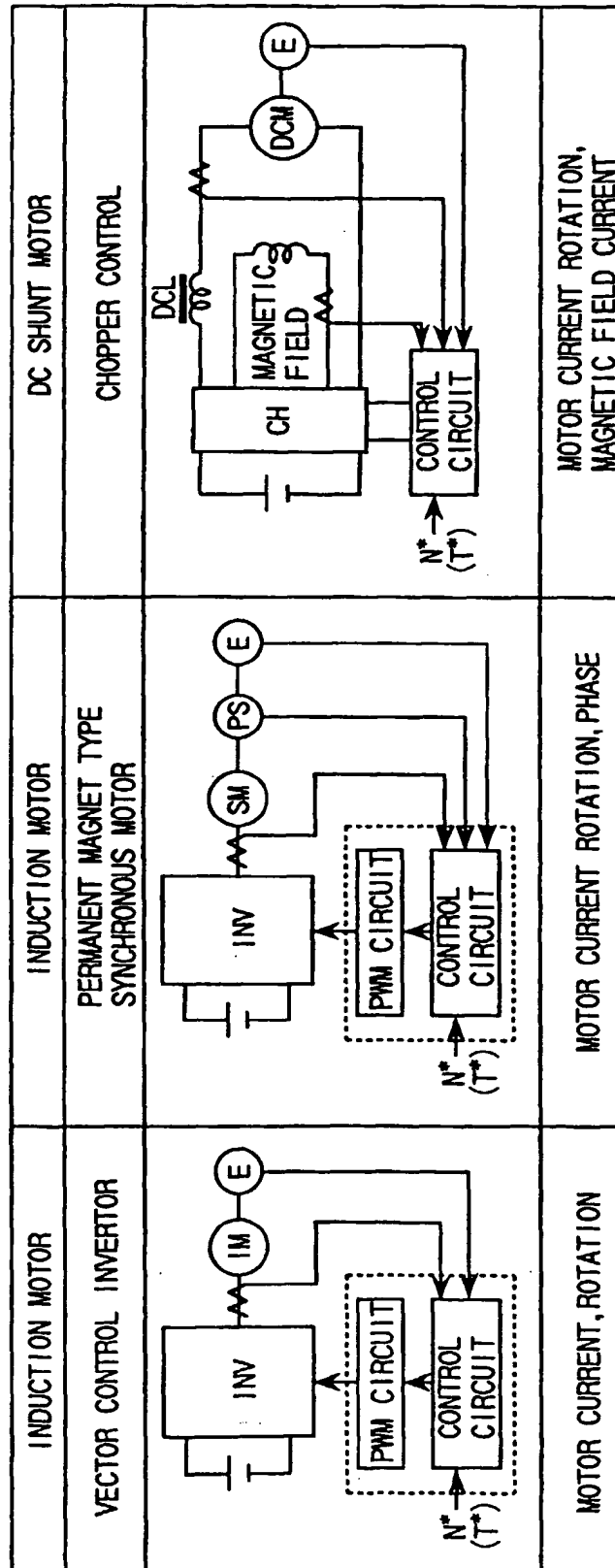
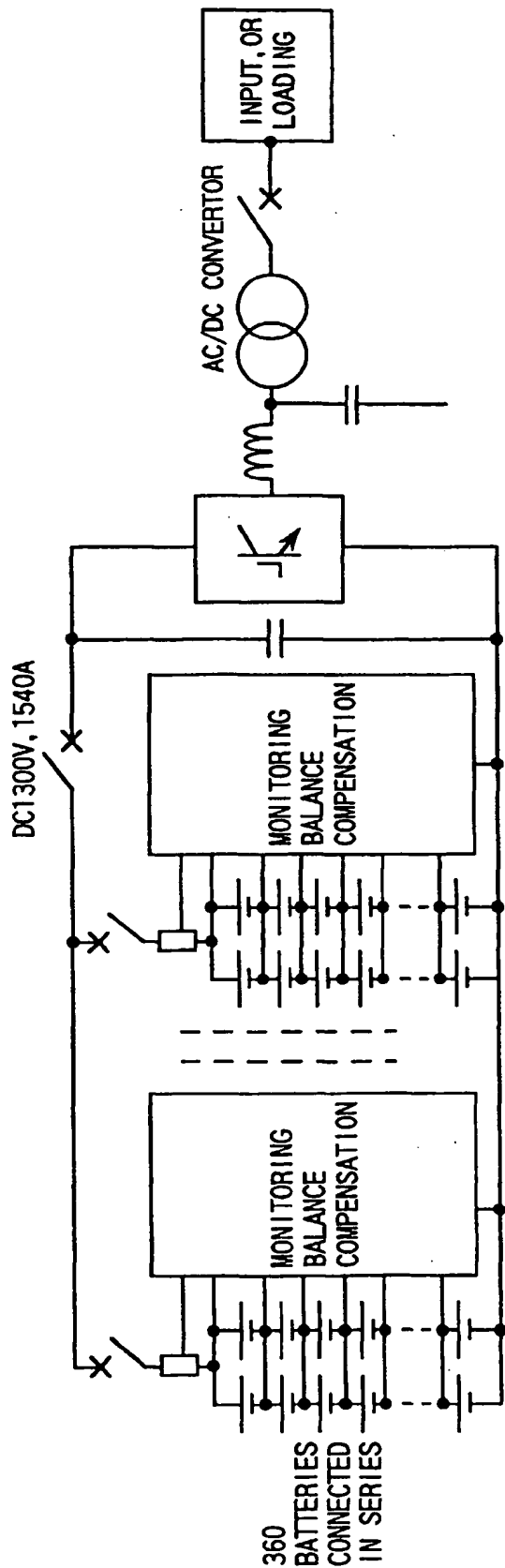


FIG.11





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 10 2880

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 614 239 A (TADIRAN LTD) 7 September 1994 * column 6, line 10 - line 55; claims 1-23 * ---	1,2,6,8, 11,13,14	H01M10/42 H01M10/40
X	EP 0 631 339 A (CANON KK) 28 December 1994 * page 9, line 15 - line 20; claims 1-22 * D,X & PATENT ABSTRACTS OF JAPAN vol. 97, no. 06 & JP 09 045369 A * abstract *	1,2,6,8, 11,13,14	
X	EP 0 814 531 A (CANON KK) 29 December 1997 * claims 1-53 * D,X & PATENT ABSTRACTS OF JAPAN vol. 95, no. 01 & JP 62 083206 A * abstract *	1,2,6,8, 11,13,14	
X	US 5 580 680 A (CHALONER-GILL BENJAMIN ET AL) 3 December 1996 * column 5, line 45 - line 55; claims 1-30 * ---	1,2,6,8, 11,13,14	TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01M
X	DATABASE WPI Section Ch, Week 9404 Derwent Publications Ltd., London, GB; Class E13, AN 94-029184 XP002106697 & JP 05 335033 A (FDK CO LTD) , 17 December 1993 * abstract * --- -/--	3	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 June 1999	Examiner Battistig, M
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EPO FORM 1503 03 82 (P04C01)



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EUROPEAN SEARCH REPORT

Application Number
EP 99 10 2880

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 286 (E-541), 16 September 1987 & JP 62 086673 A (TOYOTA CENTRAL RES & DEV LAB INC), 21 April 1987 * abstract *	4	
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 169 (E-328), 13 July 1985 & JP 60 041775 A (SANYO DENKI KK), 5 March 1985 * abstract *	3	
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Place of search THE HAGUE		Date of completion of the search 21 June 1999	Examiner Battistig, M
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21-06-1999

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FIG. 1

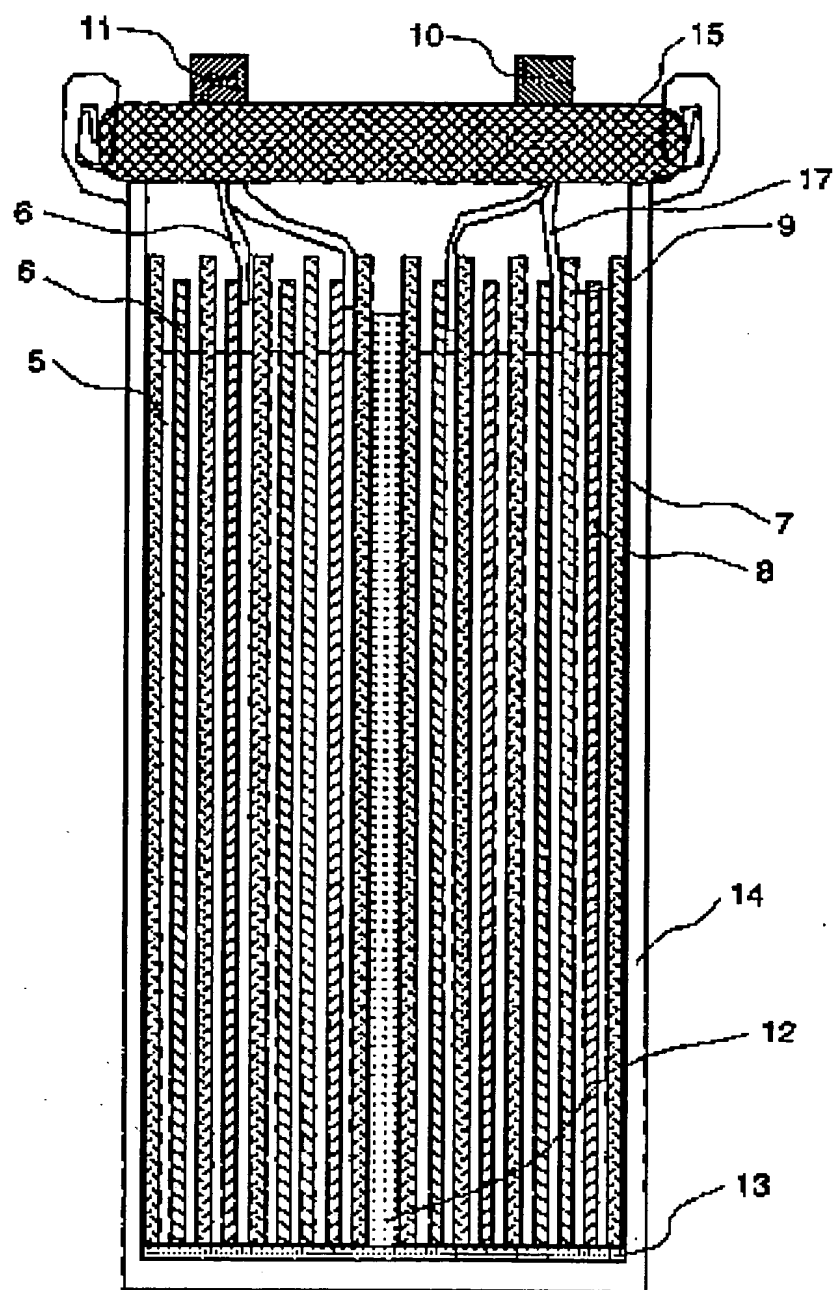


FIG. 2

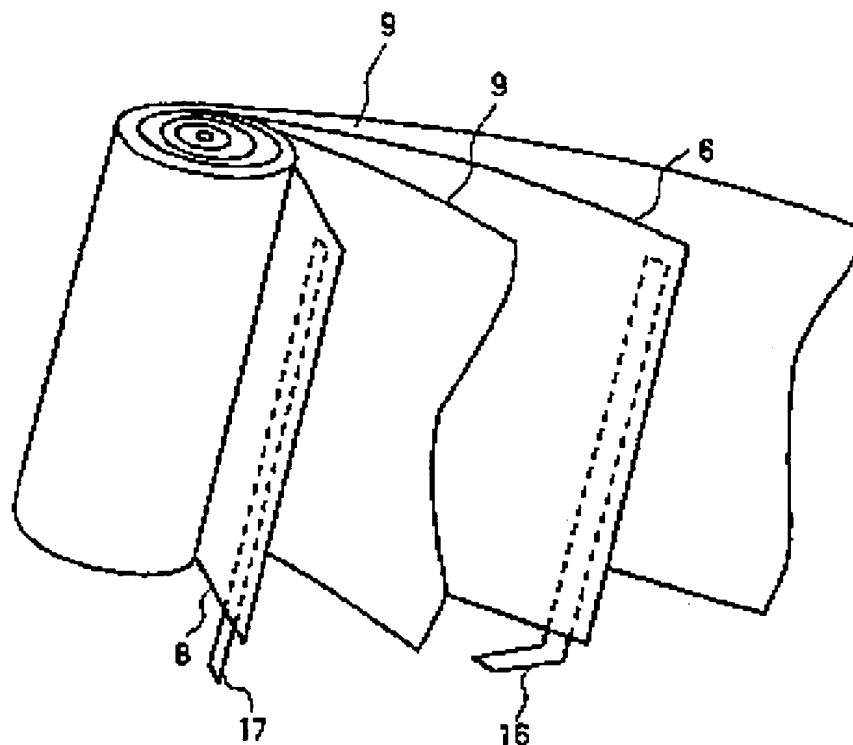


FIG. 3

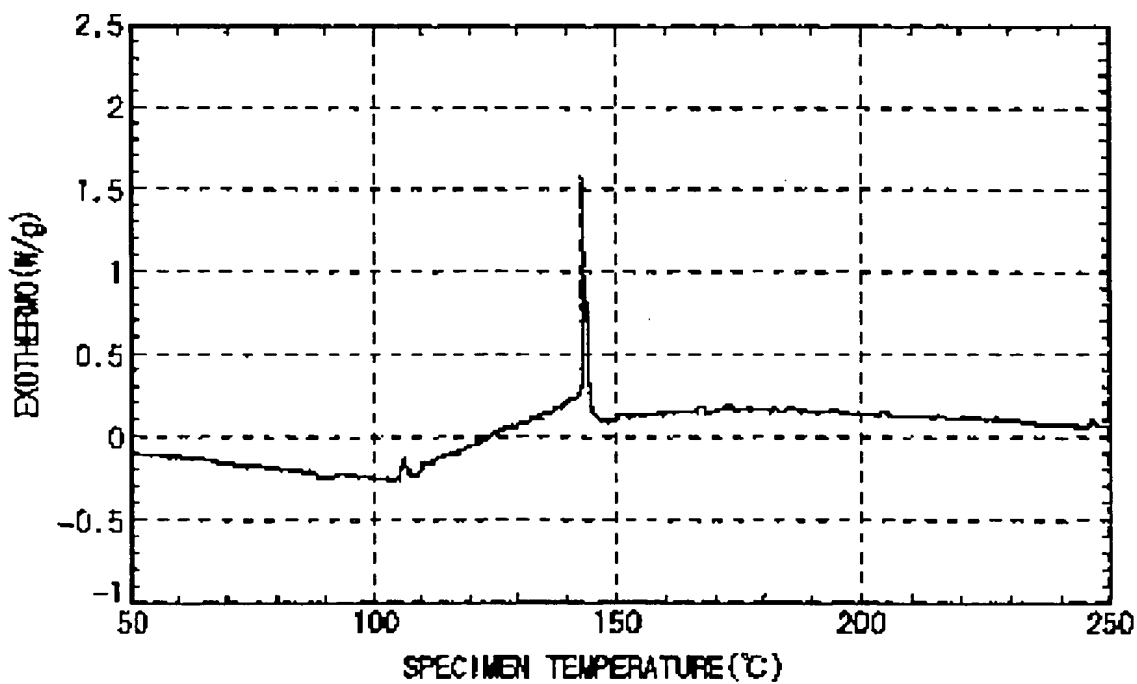


FIG. 4

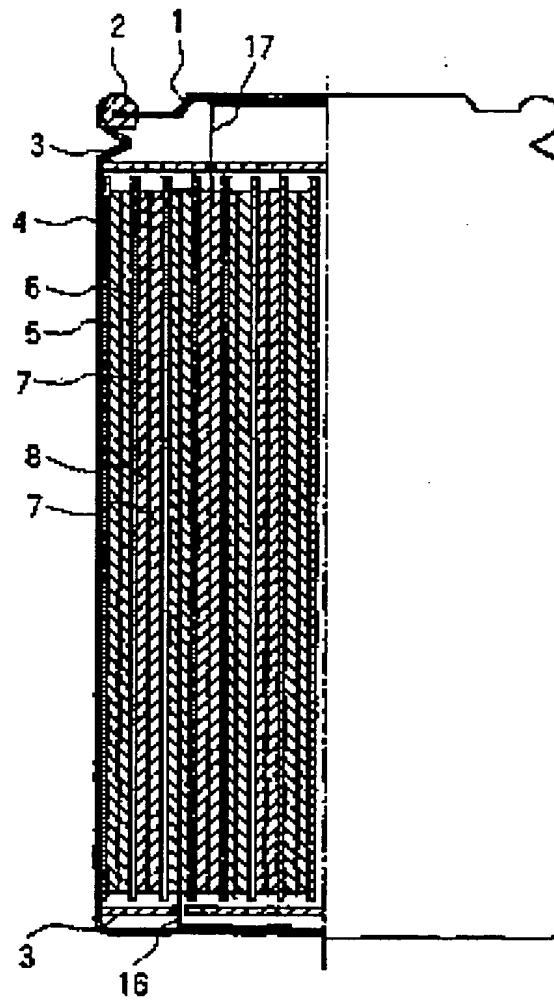


FIG. 7

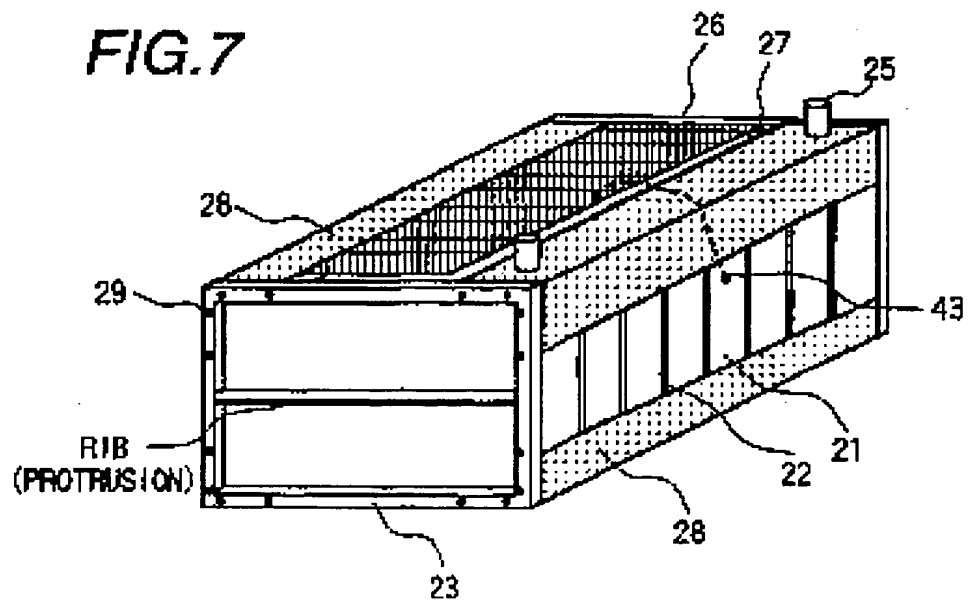


FIG.5

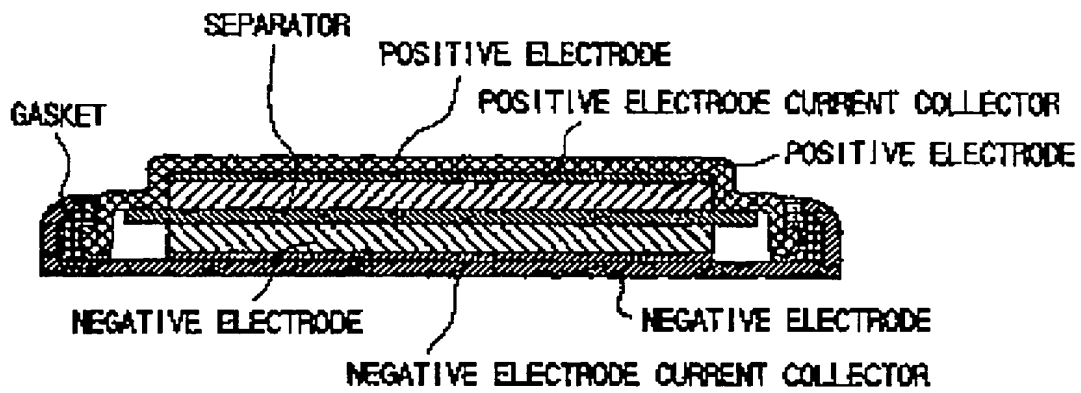


FIG.6

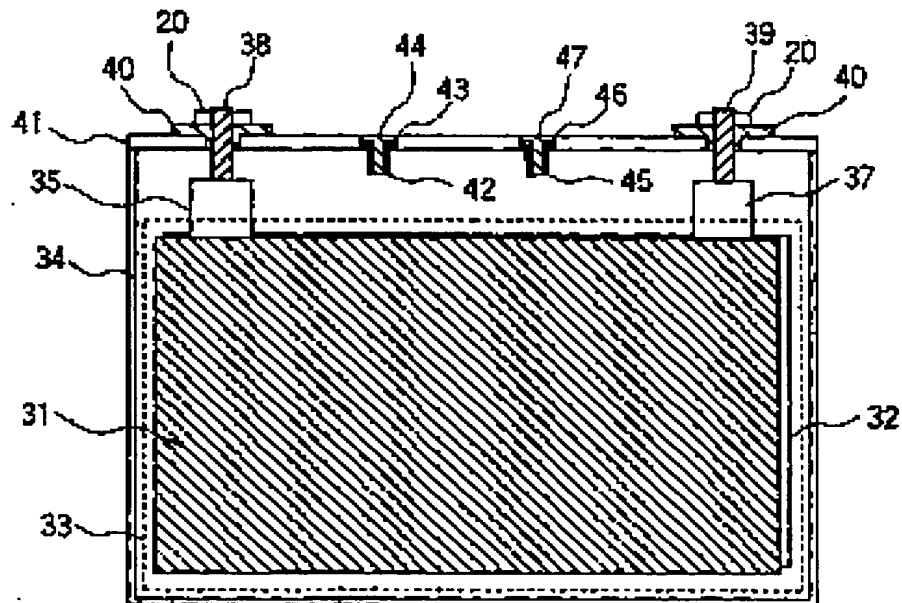


FIG. 8

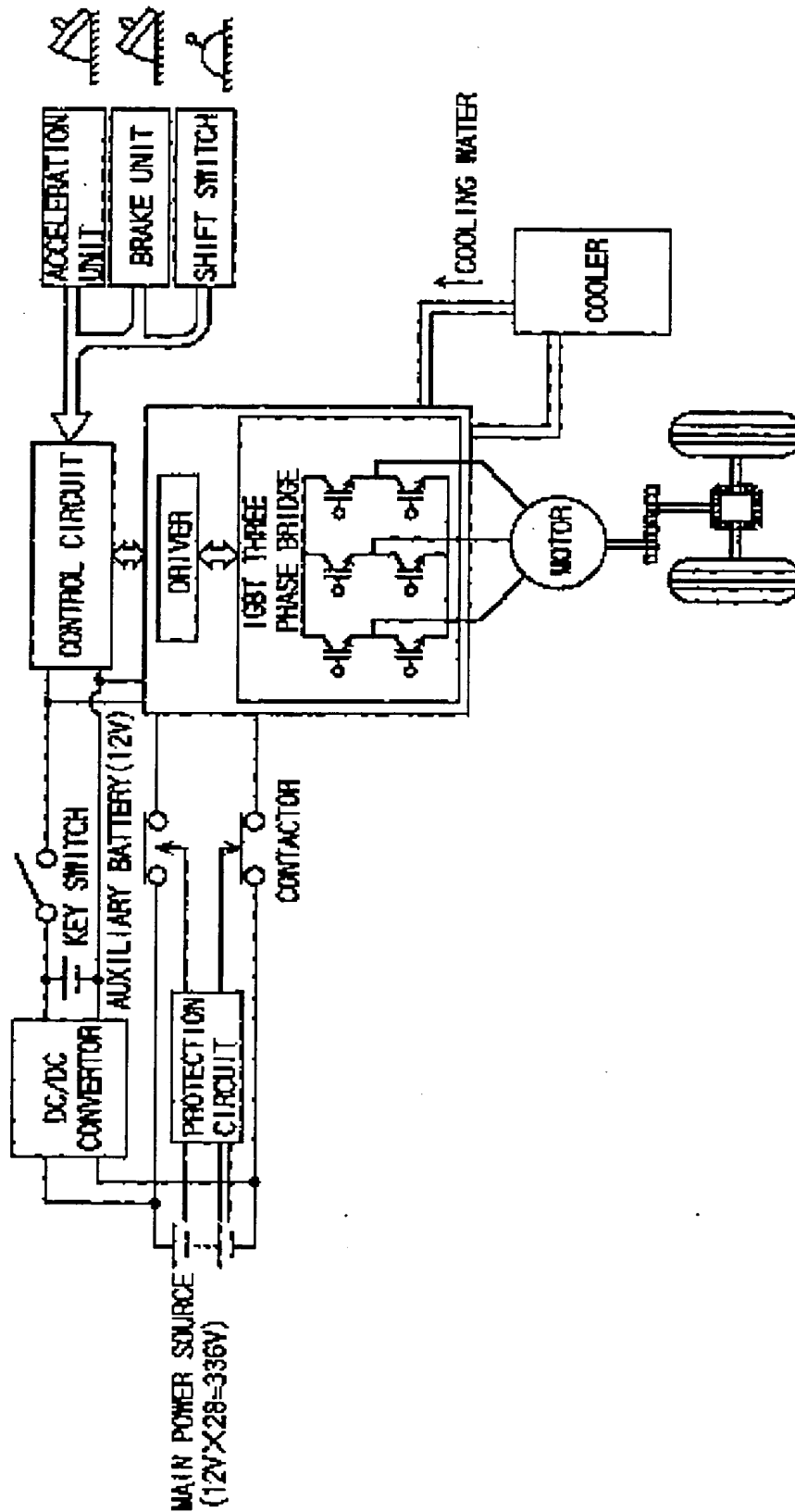


FIG. 9

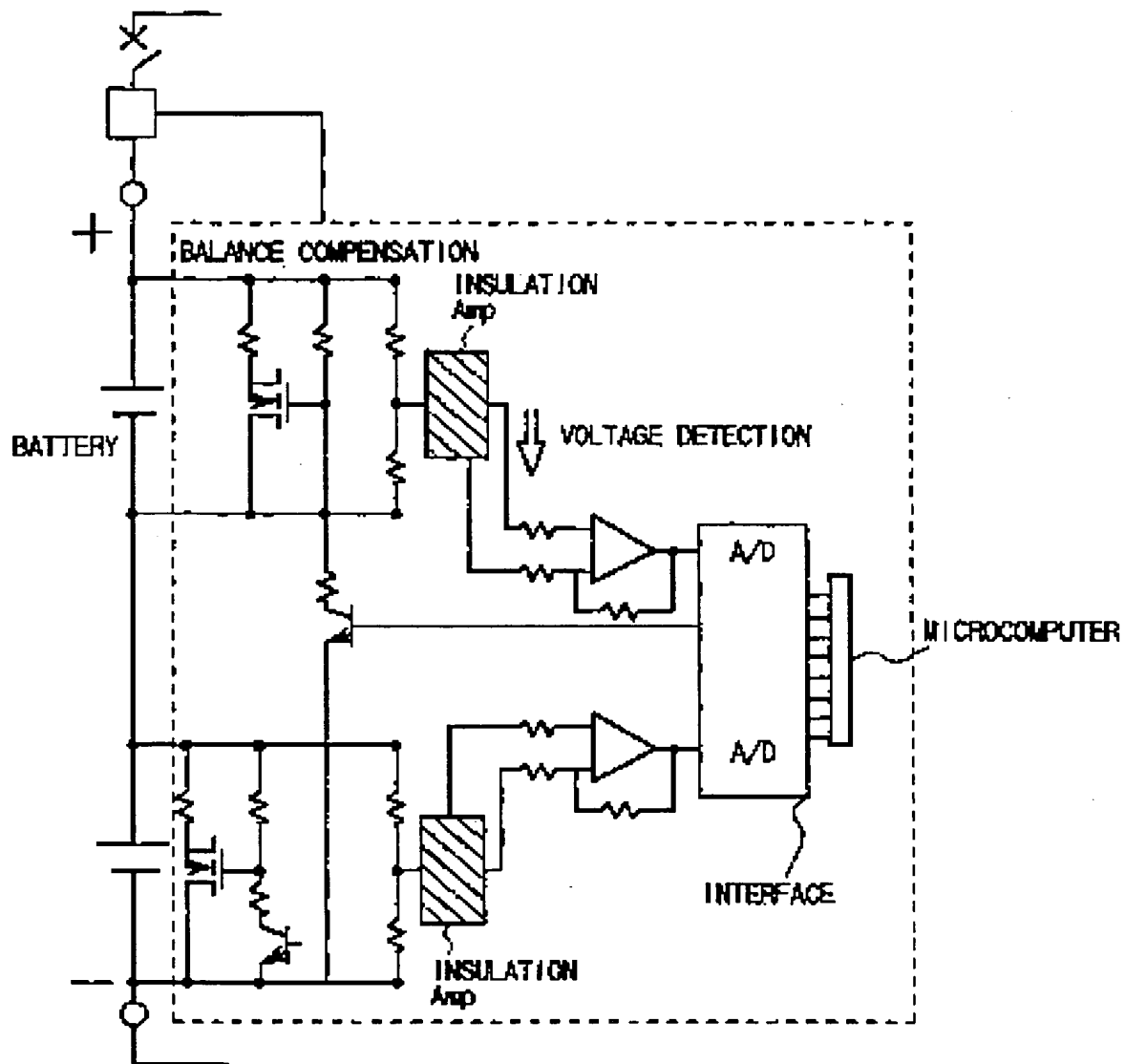


FIG. 10

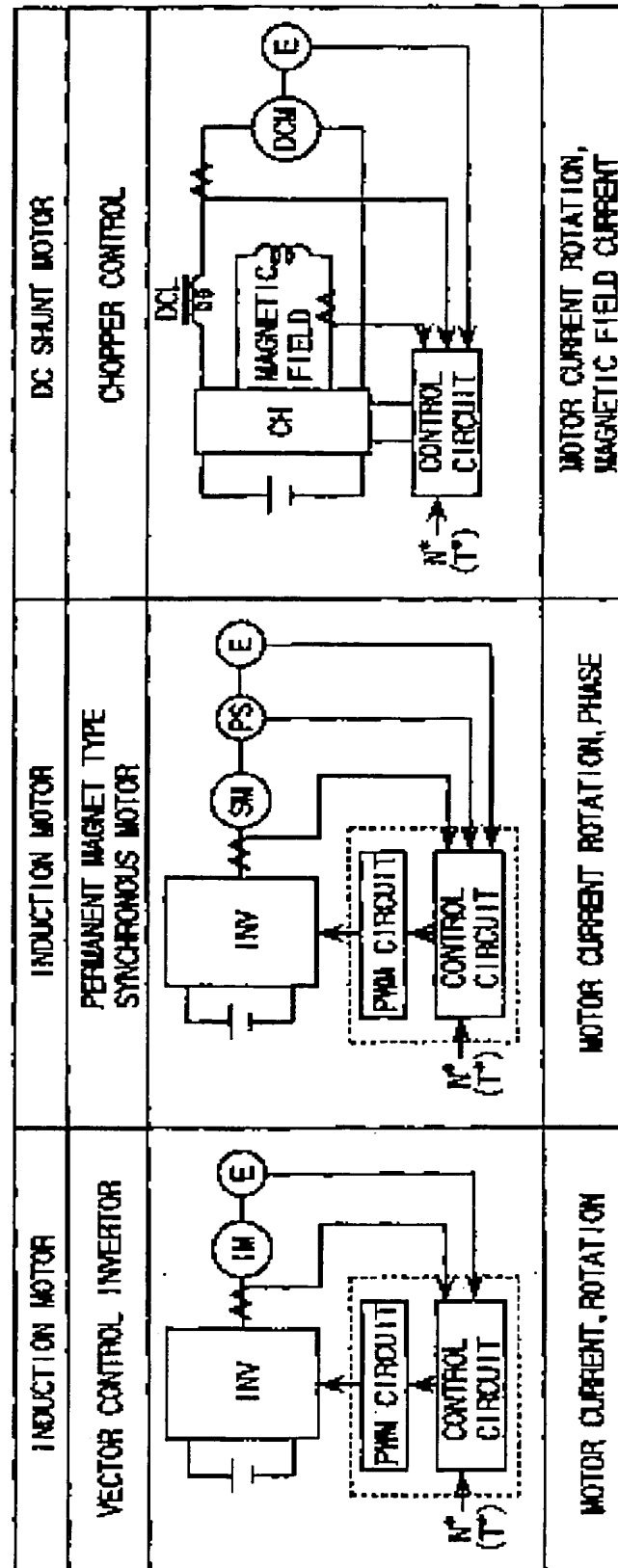


FIG. 11

